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PLANT OPERATIONS FINAL REPORT, CO₂ ACCEPTOR PROCESS
GASIFICATION PILOT PLANT

Final Report, Vol. 12, Book 3 of 4 for January 1972—October 1977

Work Performed Under Contract No. EX-76-C-01-1734

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PLANT OPERATIONS FINAL REPORT

CO₂ ACCEPTOR PROCESS GASIFICATION PILOT PLANT

**FINAL REPORT
VOLUME 12, BOOK 3 OF 4
PERIOD: JANUARY 1972 - OCTOBER 1977**

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DEVELOPMENT OF ACCEPTOR RECONSTITUTION PROCESS

6.1 BACKGROUND

As pointed out in Book 2, Section 5, the capability of a limestone or dolomite acceptor to undergo repeated carbonation in the gasifier and calcination in the regenerator is essential to the CO_2 Acceptor Process. Experience has shown that a progressive decline in acceptor activity* for carbon dioxide absorption occurs with continued use; this activity loss is attributed to the growth of calcium oxide crystal size with a consequent loss of surface area.

Accordingly, even though attrition losses are small for many stones, it is necessary to add fresh acceptor to the system and withdraw spent material to maintain constant equilibrium activity.

While natural stones that exhibit suitable physical and chemical properties for use as acceptor makeup are widespread geographically, the need for a major supply of fresh stone and the disposal of spent stone could be a severe economic detriment to commercial CO_2 acceptor gasification plants in remote locations. A significant incentive therefore exists to reduce or substantially eliminate makeup acceptor requirements.

6.2 EXPLORATORY WORK

Bench-scale studies in 1964-1970 at CCDC had shown that conversion of inactive acceptor particles to molten CaCO_3 - $\text{Ca}(\text{OH})_2$ mixtures by reaction with steam results in restoration of acceptor activity after dehydration and calcining: Two alternative processing routes were conceived and evaluated⁽¹⁾; each involved high pressures and temperatures to achieve melt formation.

A third potential alternative which was in commercial use in the pulp and paper industry was the Dorr-Oliver Fluosolids Lime-Mud Reburning System⁽²⁾. A bench-scale study of materials from Rapid City Pilot Plant was carried out by Dorr-Oliver in 1976.⁽³⁾ The processing sequence included:

- (1) Slake in hot water to convert the spent acceptor to a slurry of micron size $\text{Ca}(\text{OH})_2$.
- (2) Remove coarse (plus 200 mesh) impurities.
- (3) Dry in a rotary kiln.
- (4) Calcine and pelletize at 1650°F and one atmosphere.
- (5) Cool and collect the desired 6 x 9 mesh product; recycle oversize and undersize.

The Dorr-Oliver tests indicated that a product of acceptable activity and hardness could be made. Accordingly, a decision in early 1977 was made to produce 40 tons of acceptor for a test in the Rapid City Pilot Plant. The target date for implementation was August, 1977, to permit testing prior to termination of the pilot plant program.

*Defined as the mol ratio of active calcium oxide to the total initially useful calcium in the acceptor.

- (1) " CO_2 Reactivation and Reconstitution Commercial Economics," G. D. Rutledge, CCDC Report, Project NO. 533.50, January 16, 1975.
- (2) "Fluosolids Lime-Mud Reburning, Bulletin No. 7050F," Dorr-Oliver, Inc., 1974.
- (3) "Slaking, Size Separation and Fluosolids Reburning of Spent Lime Acceptor Product," Order No. 76052, Dorr-Oliver, Inc., June 30, 1977.

6.3 PILOT SCALE MANUFACTURE

Since No Dorr-Oliver lime reburning unit of proper size was available for use, a 24-inch fluid bed reactor owned by Hazen Research, Incorporated in Golden, Colorado, was chosen for the manufacturing phase. Hazen was selected because its personnel had some lime reburning experience, the reactor was large enough, and Golden is relatively close to Rapid City. Hazen Research did not possess equipment to dry the slaked lime at the required capacity. Consequently, the slaking, separating, and drying responsibility was contracted to the Colorado School of Mines Research Institute (CSMRI) at its Table Mountain Research Center in Golden.

Starting material for the reconstituted acceptor was a mixture of the regenerator spent acceptor dumps collected from Runs 39, 40B, 42, and 43. Velva and Glenharold lignite fines were used as fuel for the calcination and pelletizing step.

6.3.1 SLAKING, DRYING, AND PULVERIZING

The system is shown on the flow diagram, Figure 6-1. The calcium oxide was slaked in an agitated tank with water to produce a 30 to 50 percent solids slurry. Steam was supplied to the slaker to raise the temperature to 160 to 180°F. The slurry was screened to remove any oversize material. The screened slurry was dried in the rotary drier. The product was collected in 55-gallon drums. The work was done on the basis of operating five days per week and three shifts per day, at a 200-pound-per-hour feed rate.

The drier has a steel shell with lifters and was direct-fired cocurrent with a natural gas burner. Cocurrent firing was used so that any flame impingement was on the slurry or wet cake material. Thus, the maximum temperature of the dried material was below the calcium hydroxide decomposition temperature. With the lifters in the drier and cocurrent firing, any material that formed a ring was broken manually. The product from the rotary dryer was dried to zero moisture and pulverized to minus 100 mesh in a Herbert attritor. The processing rate was approximately 2,000 pounds per hour. Therefore, material produced in 24 hours of drier production was pulverized during one 8-hour shift.

Colorado School of Mines Research Institute processed 80 tons of reject acceptor from the lignite operations at Rapid City. In addition, 10 tons of reject acceptor produced while running Wyodak coal were processed. The latter material proved to be most unsatisfactory for slaking, such that higher temperatures and longer slaking times were required. The resultant slurry had a brown color, in contrast to the green slurry obtained when slaking acceptor from lignite operations.

The principal operating problem at Colorado School of Mines Research Institute was the frequent wearing out and breakage of bearings on the kiln. This kiln had a 1/2-inch inner alloy steel shell which was not part of the original design. This extra weight and misalignment of the kiln were the primary causes of bearing failure.

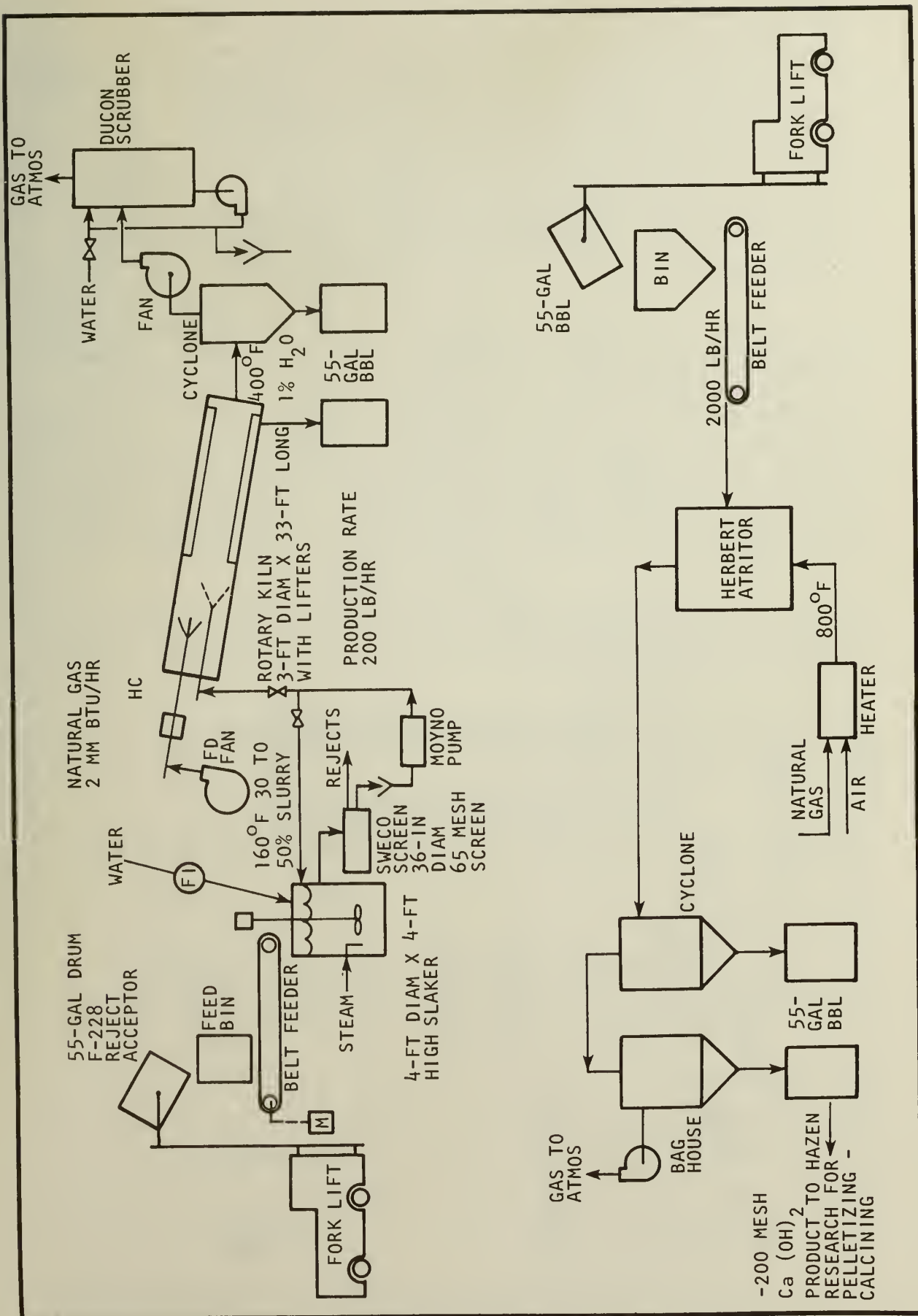


Figure 6-1. SLAKING, DRYING, AND PULVERIZING FACILITIES AT COLORADO SCHOOL OF MINES RESEARCH INSTITUTE

6.3.2 CALCINING, PELLETIZING, AND SIZING

A process flow diagram of the Hazen unit is shown in Figure 6-2. Fine calcium hydroxide particles were fed to the reactor where they calcined immediately at the 1650°F temperature. The impurities (sodium, etc.) in the feed formed a sticky substance (melt or flux) at this temperature and caused fine particles to adhere to the seed pellets in the bed. The space above the fluid bed called the freeboard was expanded in diameter to decrease the upward velocity of the gases and to allow fine solids to fall back into the bed. The fluidizing velocity was great enough (three to eight times minimum fluidization velocity) to ensure a homogeneous mixture of bed material below the freeboard. This helped to eliminate hot spots that might occur with a stratified bed.

Bed material was withdrawn through an outlet in the center of the air distributor at the bottom of the vessel. This material was conveyed by a water-cooled screw conveyor to a Size 4 Tyler mesh screen where the oversize was withdrawn. Minus 4 mesh material was further conveyed by another screw conveyor to a Size 10 Tyler mesh screen. At this point, the 4 x 10 mesh product was collected and stored. The minus 10 mesh material, spheres that had not yet grown to the desired size range, was returned to the calciner as new seed material. The oversize (+4 mesh) material was sent through an attritor where it was pulverized to a fine dust. This attrited oversize was added to the fresh hydroxide which was fed to the unit.

Fluid bed operations for the production of acceptor were initiated in March and terminated in July, 1977, when the feed supply was exhausted. A number of mechanical problems were encountered and resolved. Process problems included the following:

- (1) Uncertainty regarding the proper seed to feed ratios.
- (2) Activation of product.
- (3) Control of unit atmosphere.
- (4) Deposit formation and plugging of withdrawal system.

In general, operations improved as the tests progressed and a greater familiarity with the system was gained.

6.3.3 OVERALL MATERIAL BALANCE

As a result of this program, a total of 54,758 pounds of product was produced and shipped to Rapid City. An additional 12 barrels or about 4,000 pounds of plus 4 mesh oversize was also shipped. The overall material balance is as follows:

(1) Input to Reactor:

(a) Slaked $\text{Ca}(\text{OH})_2$, 1b	166,349	
as CaO (X 0.77), 1b		128,089
(b) CaCO_3 , 1b	8,673	
as CaO (X 0.56), 1b		4,857
Total input, 1b		<u>132,946</u>
(c) Attrited CaO recycle feed, 1b	55,184	

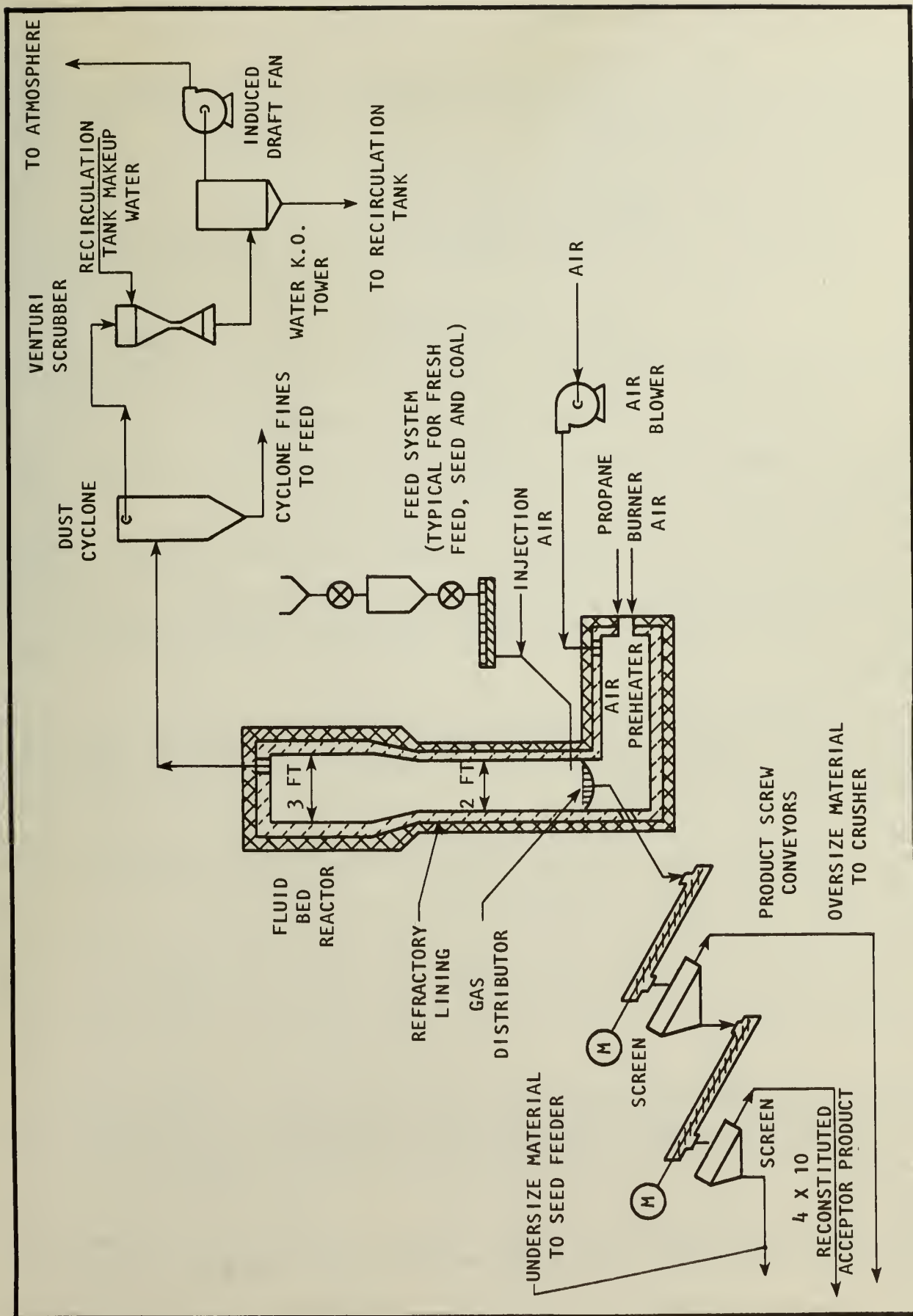


Figure 6-2. HAZEN ACCEPTOR RECONSTITUTION UNIT FLOW SCHEMATIC

(2) Output from Reactor:

(a)	Reconstituted product, lb	54,758	
	Percent of total input		41.2
(b)	Oversize, lb	4,000	
	Percent of total input		3.0
(c)	Remaining seed and cyclone dust collected, lb	18,000	
	Percent of total input		13.5
(d)	Dust to scrubber and spillage	56,188	
	Percent of total input		<u>42.3</u>
(e)	Total input, lb; percent of total input	132,946	100.0

6.4 RECONSTITUTED ACCEPTOR PERFORMANCE

Details of the performance of the reconstituted acceptor are presented in Run Report 47.⁽⁴⁾

The reconstituted acceptor was found to have an activity of 0.06-0.08; limestone acceptor typically has an activity of 0.08-0.17*. In spite of this low activity, it was possible to maintain the gasifier at a temperature about 30°F above normal without operating difficulties by increasing the acceptor circulation rates. It is clear that the spherical shape of the reconstituted acceptor permitted significantly greater showering rates than natural acceptor without upsetting gasifier operation.

While an additional, small-scale study is desirable to determine the cause for low activity in this first production sample, it is already apparent that acceptor reconstitution can be utilized to minimize concern over commercial supplies of suitable limestone and dolomites.

However, as pointed out in Subsection 5.5.4, the extent of accumulation of impurities through reconstitution and reuse must be determined to establish the necessary replacement rate with fresh stone.

(4) Run Reports-CO₂ Acceptor Process Gasification Pilot Plant Runs 43-47; Period March, 1977-October, 1977, DOE Final Report No. FE/1734-41, Vol. 8, Book 6.

*Activity not adjusted for inert (i.e., nonreactive CaO) content. Average activity for the acceptor from Run 47 was 0.091 on the normal calcium basis.

SECTION 7

QUENCH TOWER DEPOSITS

A serious problem during much of the pilot plant program was the buildup of solids in the gasifier and regenerator quench venturis, which prevented gas from being freely vented from the respective vessels. After various unsuccessful attempts to remedy the problem by relocating and redesigning the venturis, by installation of manual "rod-out" devices around the venturis, and by substitution of softened boiler feedwater for untreated potable water in the venturis, the problem was finally solved by the use of specialty chemicals supplied by Betz Laboratories of Trevose, Pennsylvania. Since different chemicals were required in the regenerator and gasifier quench systems, each system is discussed separately.

7.1 REGENERATOR QUENCH SYSTEM

After the installation of the second regenerator external cyclone, L-202A, in the regenerator overhead gas line*, the amount of suspended solids which reached the regenerator quench venturis was substantially reduced. This reduction in particle loading in the regenerator flue gas effectively reduced the solids buildup at and below the venturis that had for a long time plagued the regenerator quench system. However, deposits (though less severe) still formed and required manual "rodding" to be cleared. Samples of the deposits at the inlet of the quench tower were taken. Analyses of the samples showed that the deposits consisted primarily of calcium carbonate (CaCO_3) and other calcium compounds.

Betz Laboratories recommended the use of a crystallization inhibitor, Betz 403, in the makeup water to the regenerator quench venturi. This was initiated in Run 26B, using a concentration of about 35 PPM.

Since a crystallization inhibitor is an agent designed to minimize scaling by inhibiting the amount of precipitation of scaling constituents from solution, it was hoped that calcium compounds already present in the makeup water and those dissolved by the makeup water from the flue gas solids would remain in solution and pass harmlessly into the quench tower. When the regenerator quench venturis were inspected after shutdown of Run 26B, only minor deposits were present in the venturi throats. Process lines upstream and downstream of the venturis were clear except for a small deposit in the downstream elbow of the small venturi.

During Run 27A, Betz 429 wetting agent (basically, a surfactant-based chemical which lowers the interfacial tension between the water and the particles present and thereby reduces particle-to-particle adhesion) was also utilized in the makeup water to the regenerator quench venturis in a concentration of 12.6 PPM. The feed rate of Betz 403 was raised to 126 PPM during Run 27A. After shutdown, minor deposits were still found in the throats of the venturis, but piping upstream and downstream of the venturis remained clean.

Betz 403 and Betz 429 were used successfully throughout the remainder of the program. This problem is specifically associated with pilot plant operation; the commercial regeneration gas handling system will not include quench towers.

*After Run 22A.

7.2 GASIFIER QUENCH SYSTEM

From Run 26A (May, 1975) through Run 27C (August, 1975), Betz 403 at 126 PPM and Betz 429 at 12.6 PPM were utilized in the makeup water to the gasifier quench venturi as well as the makeup water to the regenerator quench venturi. Although this treatment did satisfactorily resolve the solids deposit problems in the regenerator quench system, identical concentrations of the same chemicals in the gasifier quench system had negligible effect. A different approach was obviously necessary.

The failure of these additives suggested that crystallization of CaCO_3 from solution was not the mechanism causing deposits. Since the product gas leaving the gasifier contained entrained calcium-based particles which could cause scaling, Betz DP-670 (a chemical dispersant designed to keep particles in suspension) was utilized in the makeup water to the venturi during Run 28A. Results were encouraging. With the concentration of DP-670 at 150 PPM, the pressure drop across the venturi stabilized at an acceptably low level and remained there throughout the run. When the gasifier quench venturi was inspected after the run, only a minor buildup was found in the diverging section of the venturi and in the piping downstream of the venturi.

During Run 28B, DP-670 was again used but at a slightly higher concentration of 200 PPM. Again, pressure drops across the venturi during the run remained at an acceptable level and subsequent inspection of the venturi after shutdown showed only minor scaling.

During the next three runs (29A, 29B, and 31), another chemical dispersant, Betz DE-427, was substituted for DP-670. With DE-427 in the system the pressure drop across the venturi remained high and often indicated the necessity to rod out the venturi. After re-introducing DP-670 to the system during Run 31, the venturi was rodded out, the pressure drop across the venturi fell to normal levels, and remained there throughout the remainder of the run.

Another approach to the problem of deposit control in the gasifier quench venturi, which was tested extensively after Run 38C, was the use of a flocculation aid (Polymer 1140) in the makeup water to the venturi. Although DP-670 had already proven effective in controlling deposits in the quench venturi, it was thought that a flocculation aid in the makeup water would promote particle agglomeration. Conceivably, larger particles would not adhere as strongly to the surfaces of the system.

During Run 39 and subsequent runs, Polymer 1140 was tested as a replacement for the considerably more expensive DP-670, and as a supplement to DP-670. Results of the tests indicated that, by itself, Polymer 1140 could slightly reduce deposits but could not control the deposit formation. However, Polymer 1140 in concentrations of 0.5 to 1.5 PPM, when used in conjunction with DP-670, would reduce the amount of DP-670 required, resulting in substantial savings in chemical costs over a long period of time.

This solution appears to be acceptable for commercial application if deposit problems arise in the gasifier quench systems.

SECTION 8

METHANATION SYSTEM AND OPERATING PERFORMANCE

As part of the OCR program to test alternative methanation systems, construction of a pilot facility was initiated at Rapid City in July, 1973, and start-up operations were begun in March, 1975. The following subsections describe the facilities, the operations, and the process performance.

8.1 METHANATION SYSTEM

The final step in SNG* production is the conversion of gasifier product gas to methane. The Rapid City methanation facility (400 Area) included facilities to remove impurities from the raw synthesis gas, a packed tube reactor cooled by Dowtherm, and an adiabatic reactor to convert final traces of carbon monoxide. Product SNG was burned in a flare.

Gas cleanup, methanation, and Dowtherm systems as used during plant operation are discussed in this subsection. Other equipment, available in the 400 Area but not used, are also briefly mentioned. A flow diagram of the 400 Area can be found in Figure 8-1. Detailed piping and instrumentation drawings are presented in the Appendices, Subsection 13.1.

8.1.1 HOT POTASSIUM CARBONATE SYSTEM

Raw synthesis gas received from the gasification section of the main facility consists of 55 to 60 percent H_2 , 13 to 15 percent CO , 9 to 11 percent CO_2 , 11 to 13 percent CH_4 , and minor amounts of sulfur compounds. Since the gas was quenched in the 300 Area, it is cool and relatively free of solids; however, most of the 9 to 11 percent CO_2 present in the gas is unnecessary to the methanation reaction. To remove the unnecessary CO_2 , the raw synthesis gas is routed through E-303, the synthesis gas CO_2 absorber. The CO_2 absorber tower is 65 feet high and 3 feet in diameter. It has three packed beds of 1-inch saddles and is supplied with lean hot potassium carbonate solution at two levels in the tower. Flow of potassium carbonate solution to the separate levels, as well as the temperature of the solution to the upper level, is controlled in the 400 Area control room. Manipulation of the amount of solution to the tower, as well as the temperature of the solution, enables the 400 Area operator to regulate the amount of CO_2 absorbed from the synthesis gas. Synthesis gas compositions out of the absorber are monitored in the 400 Area control room with on-line chromatographs.

A secondary function of the CO_2 absorber tower is hydrogen sulfide (H_2S) removal. The majority of H_2S in the raw synthesis gas is absorbed by the potassium carbonate solution. Since final sulfur removal is the next step in the gas clean-up section, the H_2S removed in the CO_2 absorber tower significantly increases the service life of the zinc oxide in D-305, the zinc oxide sulfur guard, which is immediately downstream of E-303.

*SNG - Substitute natural gas.

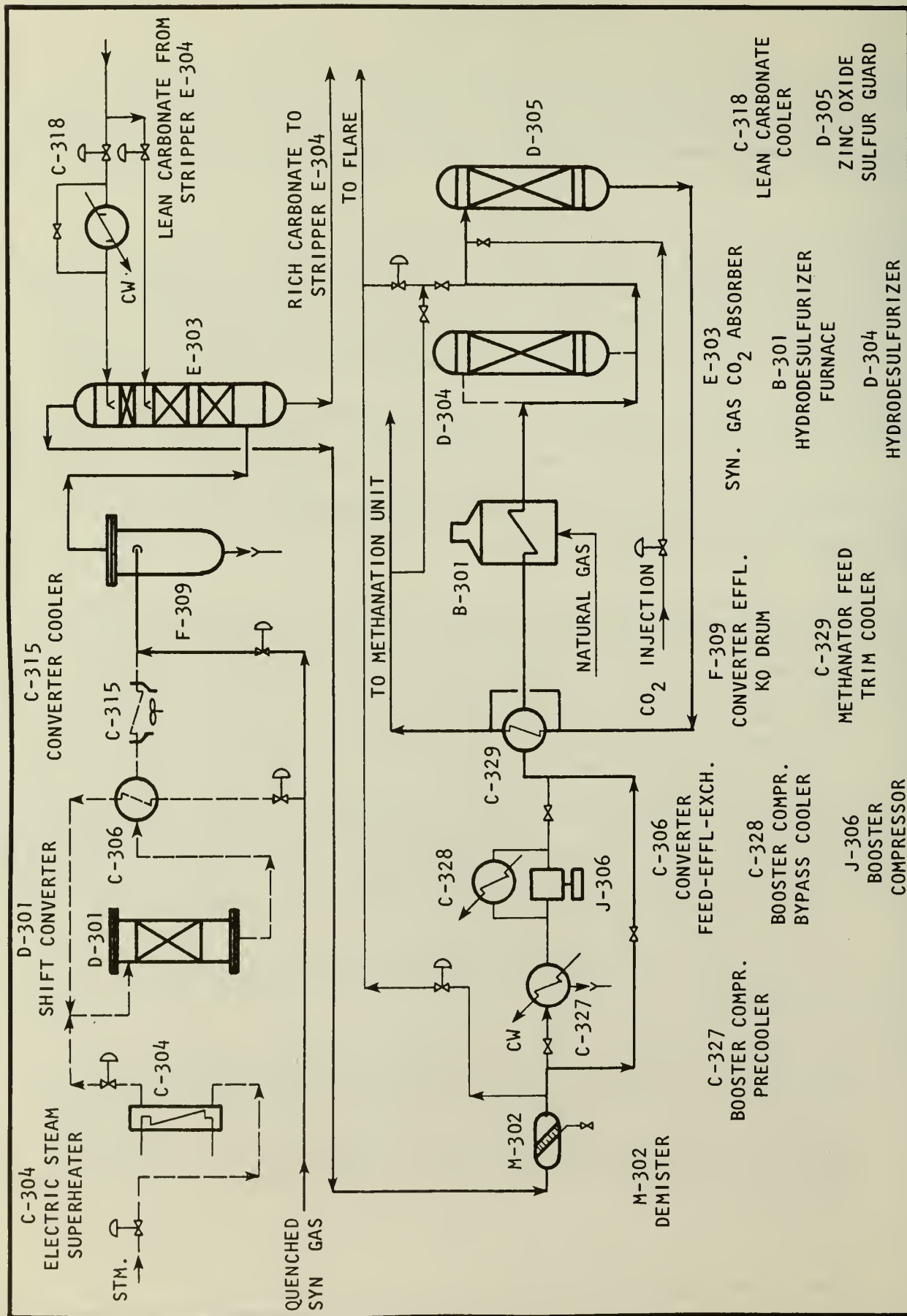


Figure 8-1. METHANATION SYSTEM (400 AREA) FLOW DIAGRAM (Sheet 1 of 2)

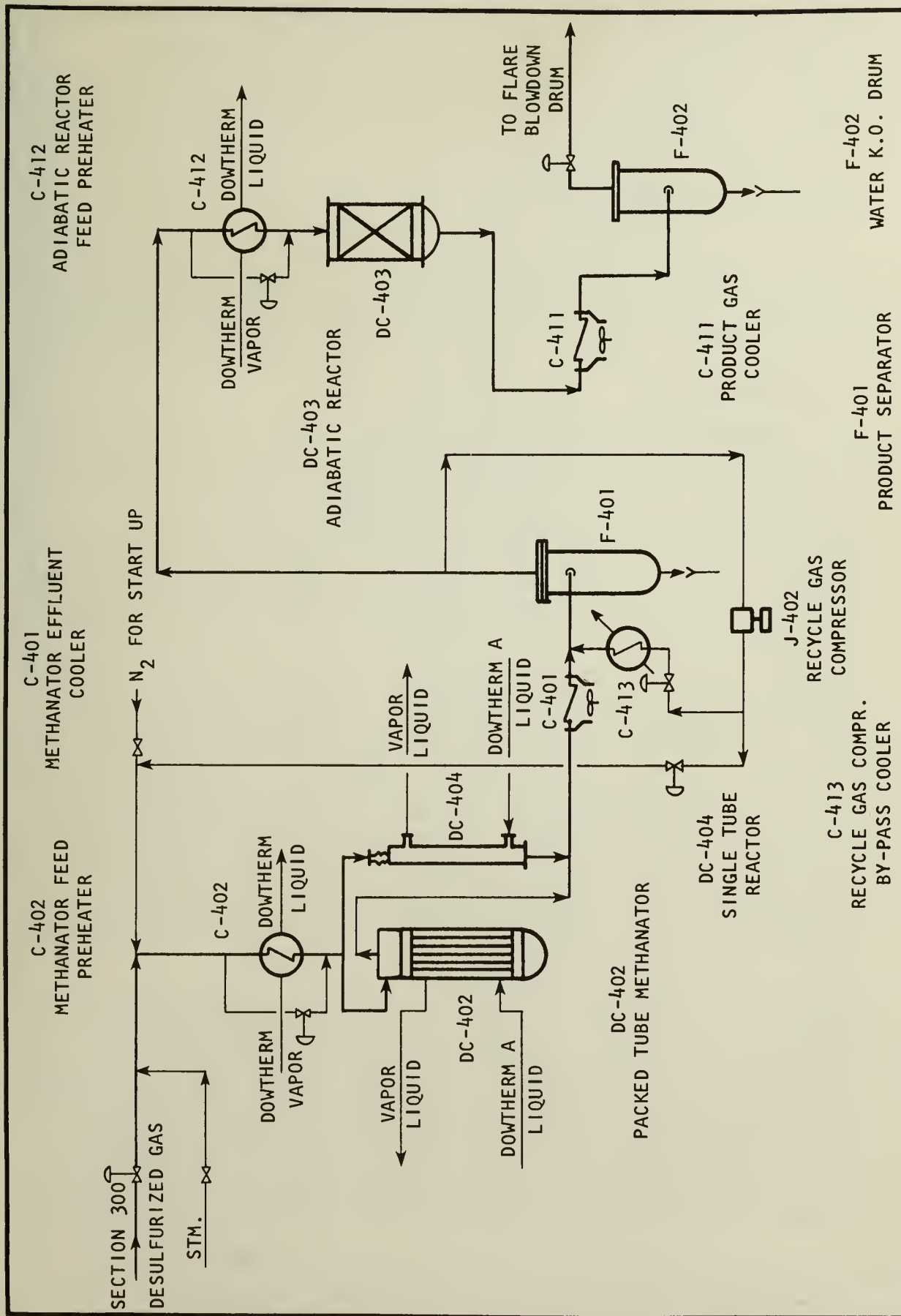


Figure 8-1. METHANATION SYSTEM (400 AREA) FLOW DIAGRAM (Sheet 2 of 2)

8.1.2 ZINC OXIDE SULFUR GUARD

After the synthesis gas leaves the CO₂ absorber tower, it passes through a demister to remove any entrained potassium carbonate solution. Following the demister, the booster compressor, J-306, is available to raise methanation pressure up to 300 psig when necessary. Normally, the compressor is bypassed and the gas is routed to the zinc oxide sulfur guard, D-305, for final sulfur cleanup. Before the gas reaches D-305, however, it is first heated to above 700°F, which is the operating temperature of the sulfur guard. The gas is heated in B-301, the hydrodesulfurizer furnace.

At 700°F operating temperature, the remaining traces of H₂S and COS are removed from the synthesis gas as it passes through the zinc oxide bed. Without this thorough sulfur removal, the nickel catalyst in the methanation reactors would quickly become sulfur poisoned.

8.1.3 METHANATION REACTORS

After the majority of the CO₂ and all sulfur compounds in excess of 0.2 ppm (total sulfur) have been removed from the synthesis gas, the gas is ready for methanation. There are three methanation reactors in the system. DC-402, the packed-tube-reactor, is the primary reactor in the system. DC-404, the single-tube reactor, is in parallel with DC-402; this was installed late in the project for test purposes. DC-403, the adiabatic reactor, is downstream of both tube-type reactors. This reactor serves as a polishing unit for final conversion of any carbon monoxide which escaped reaction in the primary reactors.

Synthesis gas from the zinc oxide bed in D-305 is mixed with methanator effluent recycle in the ratio necessary to limit the reaction in the methanator such that catalyst temperature can normally be kept below 900°F. The majority of the raw gas and recycle mixture then passes through the methanator feed preheater, C-402, where it is heated above 550°F by heat exchange with condensing Dowtherm A. A slipstream of unheated gas bypasses C-402 and is blended with the hot gas from C-402 to limit the methanator feed gas temperatures to 550°F. An automatic temperature controller is used to regulate mixing of the heated and unheated gases. After the methanator feed gas has been heated to 550°F, it is charged to the packed-tube methanator, or the stream can be split and sent to both the packed-tube methanator and the single-tube reactor. The reactors discharge to a common header.

The packed-tube reactor, DC-402, is a multitube reactor containing 160, 1-inch diameter 316 stainless steel tubes. (See Figure 8-2.) The vessel is a vertical heat exchanger with all but eight tubes filled with 5 feet of 1/8 x 1/8-inch CRG-A catalyst cylinders on top of 3 inches of 1/8-inch diameter alumina catalyst support balls. Each of the remaining eight tubes contains a thermowell located in the center of the tube. Movable thermocouples in the wells allow monitoring of tube temperature over the entire length of the tube. The space between the thermowells and the inside tube wall is filled with approximately 7 feet of catalyst on top of 3 inches of alumina support balls, to ensure equal pressure

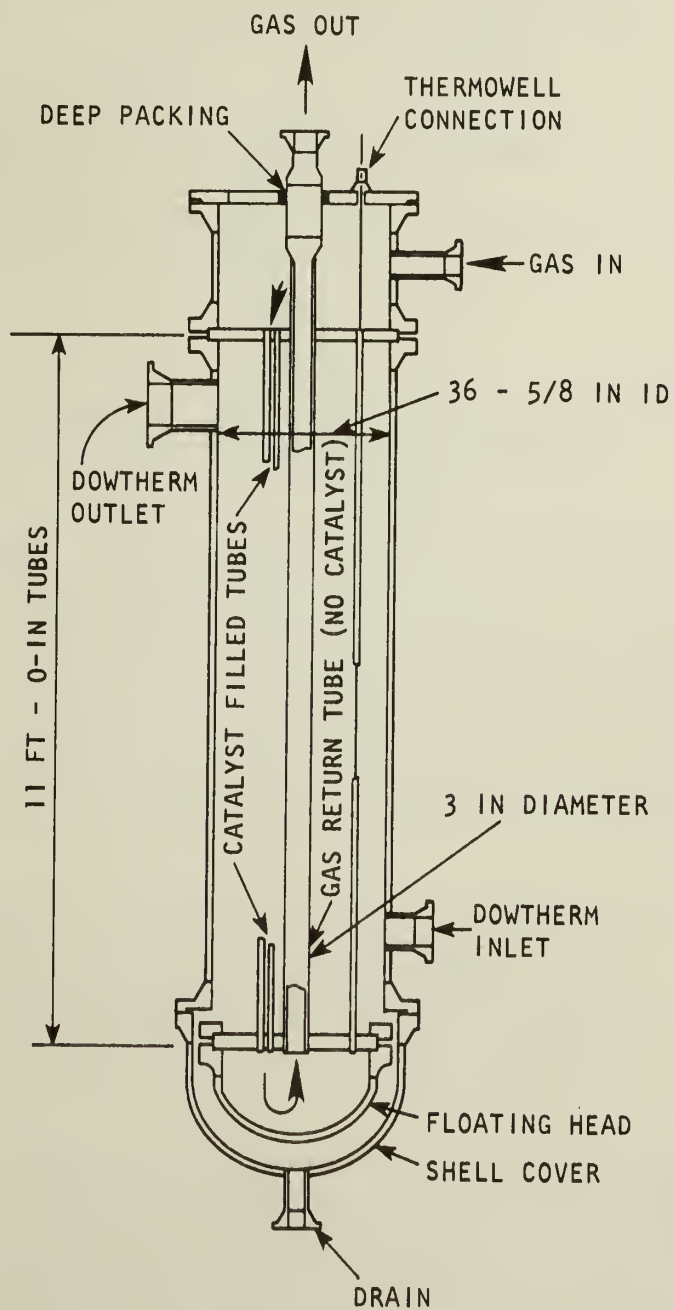
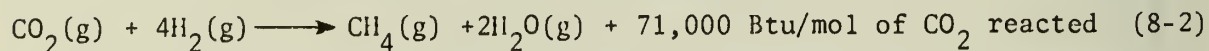
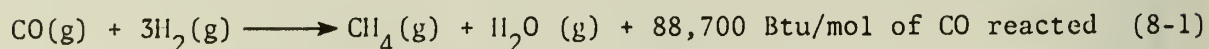


Figure 8-2. DC-402 PACKED-TUBE METHANATION REACTOR

drop across all tubes for a given gas flow rate. Additionally, when the reactor tubes were filled pressure drops were measured for each of the 160 tubes at a constant gas rate. Any tube for which the pressure drop varied more than 5 percent from the average was dumped and refilled. The pressure drop was then rechecked.

The feed gas enters the reactor and flows downward through the catalyst-filled tubes. The gases react over the nickel catalyst producing methane, water, and heat via the following overall reactions:



For convenience, reaction (8-2) is at times considered to be the combination of the reverse shift reaction



and Reaction 8-1. The reacted gases collect in the floating head section and leave through a center 3-inch diameter return tube. Boiling Dowtherm A is pumped through the shell of the reactor where it removes the heat of reaction by transfer through the tube walls.

The single-tube reactor was installed to allow comparison of reactors containing 2-inch diameter tubes with reactors containing 1-inch diameter tubes. DC-404 is simply a 2-inch diameter, Schedule 40, Type 316 stainless steel pipe which is jacketed with a 4-inch carbon steel pipe. An expansion bellows allows for differential expansion between the two pipes. Like the multitube reactor, gas passes downward through the catalyst-filled 2-inch tube. Dowtherm A, which is pumped through the annulus between the pipes countercurrent to the gas flow, removes the heat of reaction. The single-tube reactor is shown in Figure 8-3.

Reactor product gases are passed through an air-cooled exchanger and routed to a knockout pot for water removal. After the water is removed, the gas is either compressed and used as recycle or sent to the adiabatic reactor, DC-403, for reaction of any remaining carbon oxides before being vented to the flare. Product gas that goes to the adiabatic reactor is preheated in the same manner as raw gas going to the main reactors.

The adiabatic reactor is a stainless steel vessel, 6 feet tall and 18 inches wide, packed with the same nickel catalyst as the main reactors. The reactor has no internal exchange capability to remove heat of reaction, since most of the exothermic reaction should have occurred in packed-tube reactors. Any unconverted carbon oxides from the packed-tube reactors are methanated in the bed of the adiabatic reactor; the heat evolved is carried away with the gases as they leave. Gas from this adiabatic reactor is cooled in an air-cooled exchanger and sent to a knock-out pot for water removal. The product gas is then vented from the system to the flare through a pressure control valve.

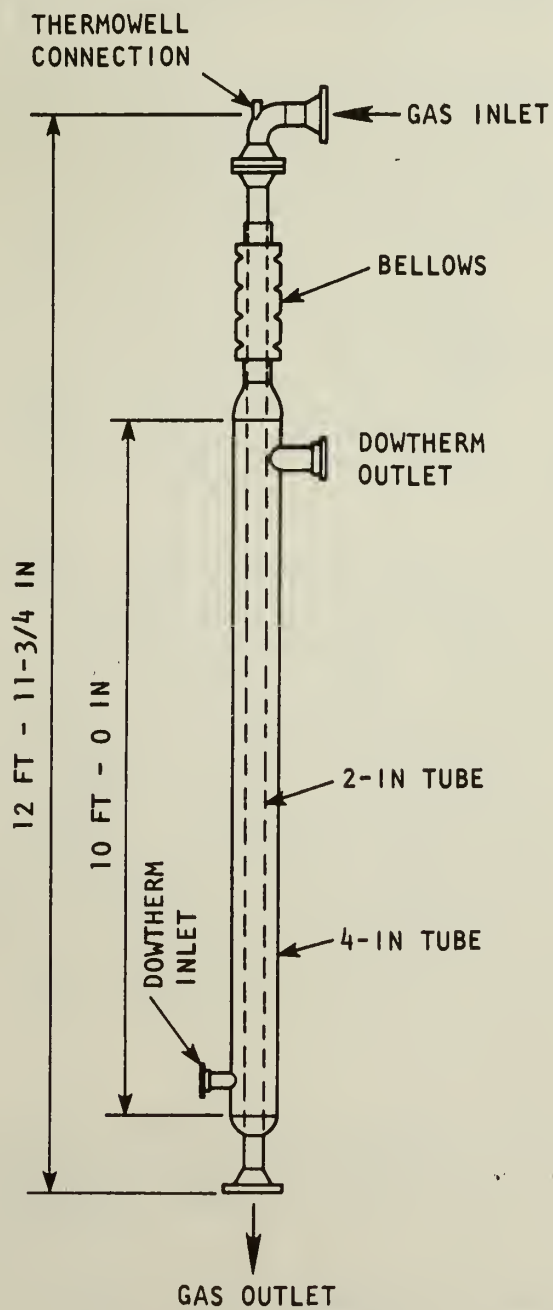


Figure 8-3. DC-404 SINGLE-TUBE METHANATION REACTOR

Figure 8-4 shows the Dowtherm system. Dowtherm A is the heat exchange medium used in the 400 Area to remove the heat from the packed-tube reactors (single-tube reactor not shown), as well as to provide heat to the feed preheaters. When methanation is not taking place, the entire system is kept warm by the Dowtherm vaporizer, B-401. When the system is operating, the cooling and heating portions of the system are isolated and operated independently of each other.

The Dowtherm A used in the packed-tube reactor is held in the Dowtherm expansion tank, F-407. Dowtherm A is pumped from the expansion tank by one of two electric pumps to the reactors. On the way to the reactors, an air-cooled Dowtherm exchanger is available in the event that circulation of subcooled Dowtherm liquid is desired for heat transfer studies. (This mode of operation was never tested.) In the shell of the reactors, the Dowtherm absorbs the heat of reaction and will, with the correct pressure and temperature, partially vaporize. The hot liquid-vapor mixture is then returned to the expansion tank where the vapors rise to the top of the tank and enter an air-cooled exchanger. In this cooler, condensation of vapors occurs and the liquid then returns to the expansion tank via gravity. By controlling the rate of heat removal, the rate at which vapor is condensed can be controlled, and the temperature and pressure of the Dowtherm in the expansion tank can be regulated.

The other part of the Dowtherm system which provides heat to the methanator feed preheater, C-402, and the adiabatic reactor feed preheater, C-412, operates entirely by natural circulation, as opposed to forced circulation. When it is necessary to operate these preheaters, the Dowtherm vaporizer, B-401, is isolated from the expansion tank. A liquid Dowtherm level is established in the vaporizer. Once the vaporizer is isolated, all inerts (gases other than Dowtherm) are vented from the system at the preheaters, which are the highest points in the system. As soon as the inert gases are vented, hot vapors from the boiling liquid Dowtherm in the vaporizer migrate to the preheater, release their heat of vaporization, and condense back to a liquid without changing temperature. The liquid then flows by gravity back to B-401 where it is again revaporized. The system allows large amounts of heat to be transferred at a load-dependent rate without the use of circulation pumps. Once the system is operating, temperature control of the vaporizer is all that is necessary.

When the 400 Area was constructed, two pieces of equipment were installed but were never operated. These were the shift converter, D-301, and the hydrosulfurizer, D-304, and are shown in Figure 8-1.

The 400 Area was designed before the main plant had demonstrated that a synthesis gas could be produced with a hydrogen-to-carbon monoxide ratio of 3 or greater. Attempts to methanate gases containing lower $H_2:CO$ ratios would have resulted in the deactivation of the methanation catalyst due to carbon deposition and the production of nonpipeline quality gas due to excess carbon monoxide content. To avoid these possible problems, a gas shift converter, D-301, was added to the design. Later, when the raw synthesis gas proved hydrogen-rich, shift conversion became unnecessary.

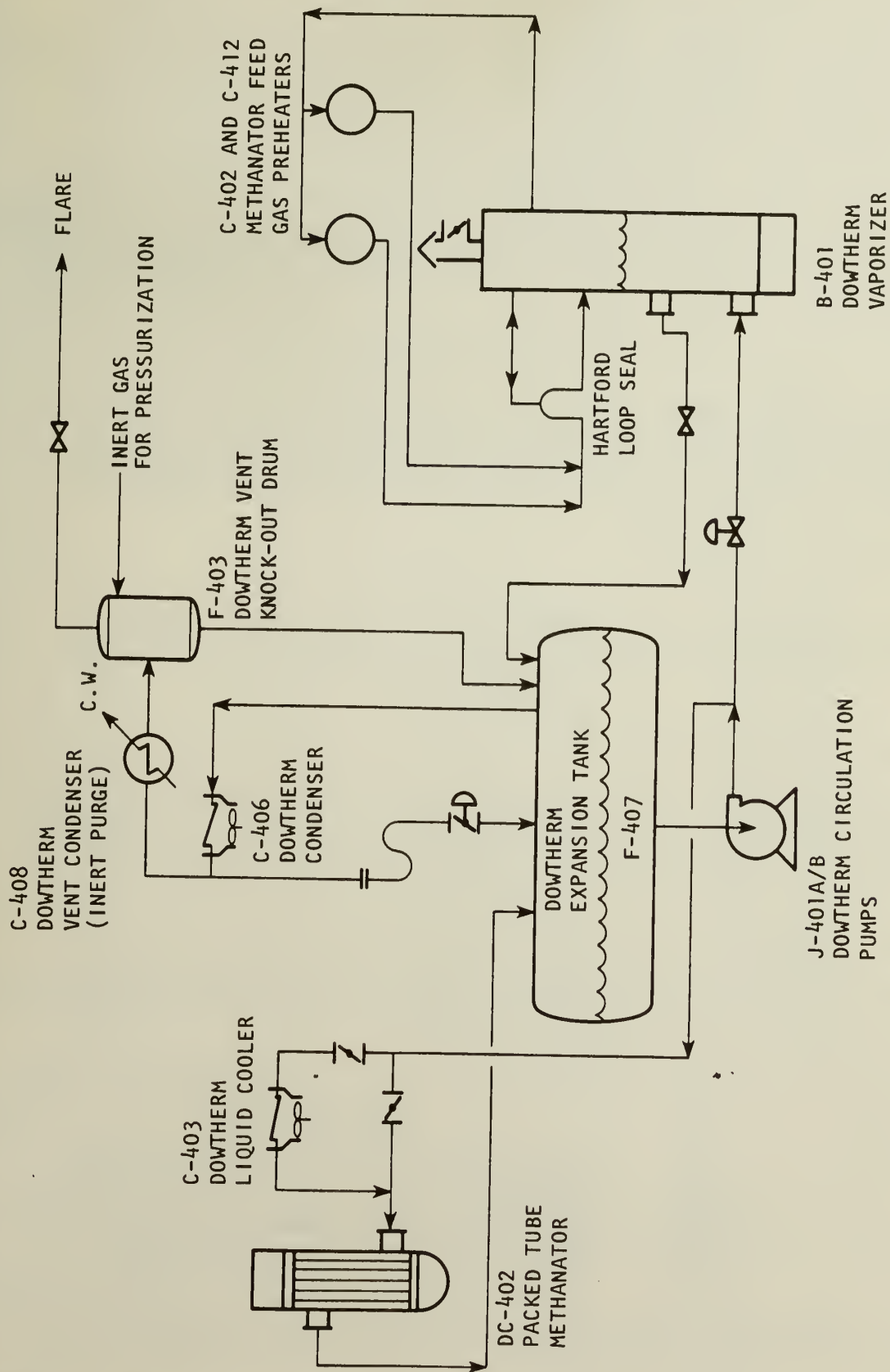


Figure 8-4. METHANATION UNIT DOWTHERM SYSTEM

When the 400 Area was designed, the amounts and types of sulfur compounds (especially organic species) in the quenched synthesis gas were not well known. Since the nickel catalyst in the methanator reactor is extremely sensitive to sulfur poisoning, a hydrodesulfurizer, D-304, was provided to convert all sulfur compounds that might be present to H_2S . The H_2S could then be completely and reliably removed in the zinc oxide sulfur guard. Fortunately, only H_2S and COS were found in the synthesis gas, so operation of the hydrodesulfurizer was never required. Because the synthesis gas from the carbonate tower contains a large amount of hydrogen (typically 60 percent) and moisture (typically 3-10 percent), conditions in the zinc oxide unit are favorable for the conversion of the COS to H_2S via hydrogenation and hydrolysis reactions. Therefore, the COS is also effectively removed by the zinc oxide unit.

8.2 METHANATION RUN HISTORY

The methanation test operations were relatively brief by virtue of the limited time schedule and the occasional lack of synthesis gas feed because of problems in gasification. Nonetheless, the methanation system operated successfully and provided definitive information on this processing concept.

8.2.1 HISTORY OF OPERATIONS

The following table (8-1) summarizes the history of operations. Twelve runs were completed for a total operating time of 920 hours.

8.3 OPERATING RESULTS

8.3.1 DETAILED OPERATING DATA

Detailed data from the methanation operations are presented in the individual run reports (DOE Final Report, No. FE/1734-41: Volume 8, Books 4, 5, and 6.) Selected run periods are presented here to illustrate typical modes of methanator operation.

8.3.2 HEAT AND MATERIAL BALANCES FOR SELECTED RUNS

Figure 8-5 presents the methanation equipment and identification numbers of streams involved in the calculations.

Tables 8-2 through 8-7 present results from the following run periods:

Table	Run	Operating Mode
8-2	33B	Packed Tube Reactor, 114 Hours On-Stream
8-3	33B	Packed Tube Reactor, 143 Hours On-Stream
8-4	33B	Packed Tube Reactor, 200 Hours On-Stream
8-5	47B	Packed Tube Reactor, Zero Recycle Gas
8-6	47B	Packed Tube Reactor, Zero Recycle Gas
8-7	47B	Packed Reactor and Single-Tube Reactor

The data exclude adiabatic reactor operation, since essentially no reaction occurred in this unit.

8.2.1

METHANATION UNIT RUN HISTORY

Run No.	Date	Hours of Operation	Problems Encountered	Results of Operation
298	11/15/75-11/17/75	50	Carbonate tower operation too efficient in removing CO ₂ from Quenched Synthesis gas. Methanated product gas, therefore, contained large quantities of hydrogen which reduced product gas heating value.	Reduced methanation catalyst. This was first attempted integrated operation of methanation unit. All process equipment operated successfully in satisfactory manner.
338	2/12/76-2/21/76	212	No major problems encountered.	Methanation unit successfully operated for long periods at steady-state conditions. Product gas with heating value of over 900 Btu/SCF was routinely produced.
36	5/7/76-5/13/76	0	--	Catalyst in packed tube reactor, DC-402, replaced & reduced. Catalyst recharging was necessary because valve switching operation after Run 338 caused reverse gas flow through reactor which blew some catalyst backwards out of tubes. Run not of sufficient duration to allow collection of meaningful heat & material balance data.
378	6/12/76-6/13/76	22	Run ended prematurely due to upset in main gasification section.	Packed tube methanator, DC-402, operated with recycle:feed gas ratio of 1.4:1. After run operated methanation unit in manner which allowed determining heat losses from system without complication of methanation reactor occurring.
39	9/10/76 9/28/76-9/30/76	2 51	Dowtherm circulation pump, J-401A, developed seal leak.	Methanator put on-stream & taken off-stream 3 times during run due to upsets which originated in main gasification section. Because of unsteady-state nature of methanator operation, meaningful process data not obtained. Successfully operated methanator, DC-402, at recycle to feed gas ratios as low as 0.56:1.
42	2/7/77	12	Dowtherm condenser, C-406, developed leaks in tube sheet header.	Operated reactor, DC-402, at recycle to feed gas ratios as low as 0.41:1. Stable operation of unit allowed sampling of several methanation process streams for iron & nickel carbonyls.
43	3/7/77-3/10/77	66	Recent newly installed on-line gas chromatographs failed to function properly due to plugged sample lines & electronic problems. After run, leaks discovered in Dowtherm condenser tube sheet header.	Run not of sufficient duration to provide meaningful process data.
44A	4/27/77-4/30/77	69	New orifice installed to more accurately measure condensed Dowtherm drain rate from C-406. However drain rate exceeded expected capacity during much of run. Flow measuring instrument rearranged near end of run.	Operated system under steady-state conditions at normal operating pressure of 98-118 psia. This allowed sampling of 5 major process streams for iron & nickel carbonyls. Operation of booster compressor checked & methanation successfully achieved at system pressure of 280 psia. During high pressure operation, methanated product gas had low heating value of only 525 Btu/SCF due to high nitrogen content of feed synthesis gas.
44B	5/15/77-5/16/77	25	--	Reduced catalyst in newly installed single tube methanation reactor, DC-404. Successfully demonstrated operation of single tube reactor system. Was first run which on-line process gas chromatographs were reliable.
45	5/31/77-6/2/77 6/5/77-6/6/77 6/6/77-6/8/77 6/9/77-6/10/77	56 9 46 29	Seal leaks developed on Dowtherm circulation pumps, J-401A&B. Leak found on booster compressor, J-306, piston rod shaft seal. Several leaks developed in Dowtherm condenser, C-406, tube sheet header.	Single tube methanator, DC-404, & multi-tube methanator, DC-402, were operated in parallel for 12.5 hrs at nominal operating pressure of 275 psig. However, operation not of sufficient duration to provide useful heat & material balance data.
46C	8/4/77-8/7/77 8/7/77-8/8/77 8/8/77-8/10/77	66 17 24	Dowtherm pump, J-401A, developed seal leak.	Successfully operated packed tube reactor without supplying recycle gas for cooling. Once-through methanation (complete methanation in single reactor with effluent CO concentrations below the 1000 ppm pipeline specification) was demonstrated. Performed variable study of effect of several feed gas rates on reactor operation. Performed comparison tests between single tube, DC-404, & multi-tube, DC-402, reactors. After run operated system to again measure heat losses without the complication of methanation reaction occurring.
47A	9/5/77-9/16/77 9/6/77-9/7/77	17 19	Difficulties experienced in bringing booster compressor, J-306, on-line. Problem was malfunctioning pressure switch. Dowtherm vaporizer, B-401, continually shut down. Vaporizer developed leaks due to warped tube sheet.	
47B	9/27/77-10/1/77	80	Temporary repairs to B-401 Dowtherm vaporizer were not sufficient to prevent tube sheet from leaking. Changes in operating procedure devised which allowed vaporizer operation to be abandoned.	

Table 8-1. METHANATION UNIT HISTORY OF OPERATIONS

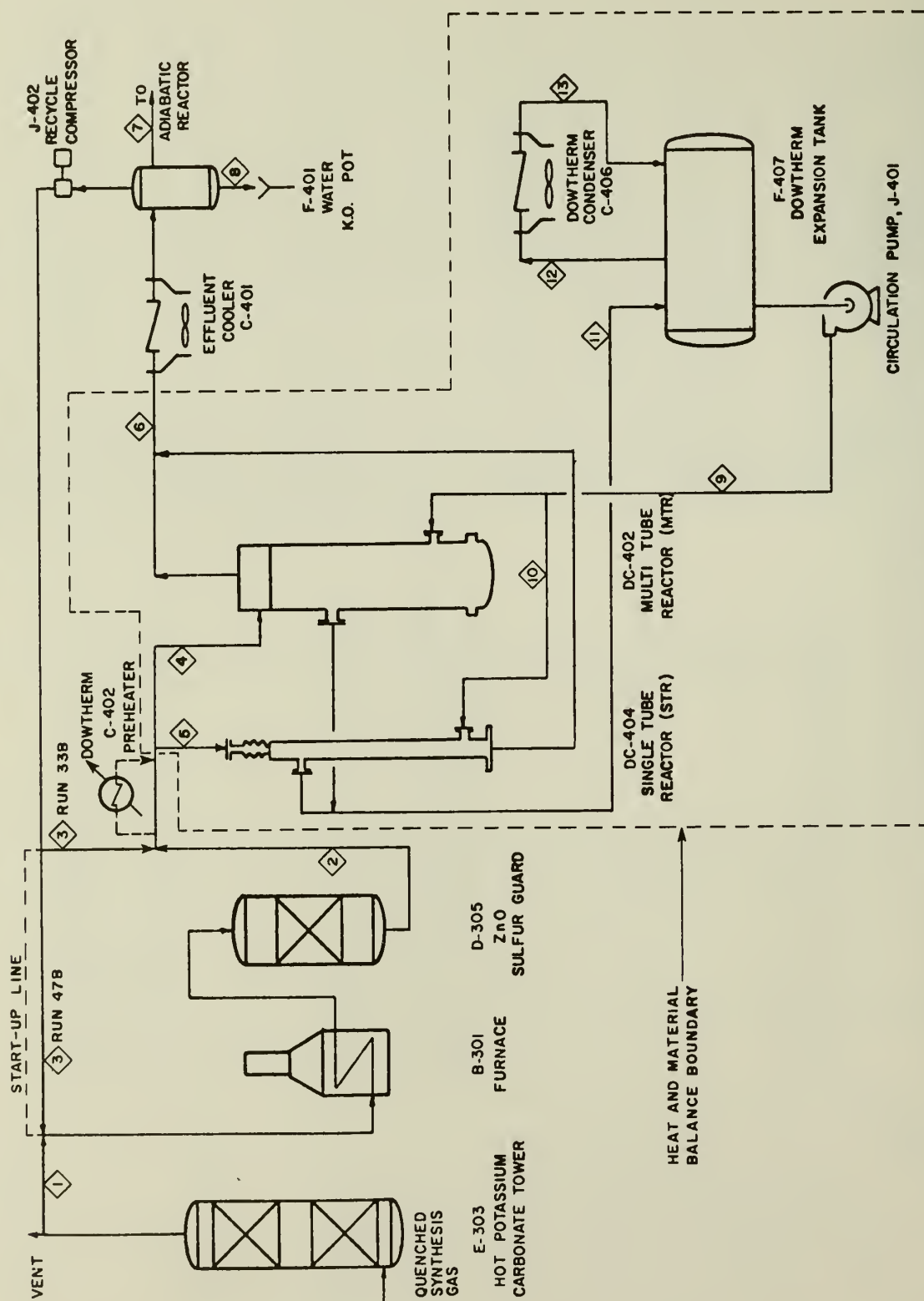


Figure 8-5. METHANATION UNIT FLOW DIAGRAM

Total (Out-In) X 100 IN														(205.00)	
Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	1,620.97	
SCFH (LB/HR)															
Dry Gas	21,534	22,036	33,552	55,588	0	41,368	7,816	0							
H ₂ O	2,176	1,674	110	1,784	0	7,625	26	(356)							
Dowtherm A									(77,410)	0	(77,410)	(2,556)	(2,556)		
Temperature, °F	205	648	162	549		537	67	67	544	-	557	551	483		
Pressure, PSIG	113	111	150	98		87	87	87							
Composition, Mol %															
H ₂	62.53	63.38	3.20	27.06		3.20	3.20								
N ₂	4.45	4.35	7.95	6.52		7.95	7.95								
CO	14.66	12.05	0.00	4.78		0.00	0.00								
CH ₄	13.96	13.64	88.85	59.04		88.85	88.85								
CO ₂	4.40	6.58	0.00	2.61		0.00	0.00								
HHV, BTU/SCF	391	382	908	699		908	908								

2/18/76 2300 HRS-2/19/76 1400 HRS
 Datum: Liquid H₂O @ 77°F

IN	LBS/HR	SCFH	PSIG	°F	Moles				Heat Content, MBTU				
					H	N	C	O					
Methanator Feed Gas													
Dry Gas	1,950	51,695	97	556	386.24	19.08	88.04	14.76	580.33				
Steam	85	1,786	97	556	9.42			4.71	107.78				
Heat of Reaction									623.03				
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ 88,700 BTU/LB Mole									274.77				
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ 71,000 BTU/LB Mole													
Total	2,035				395.66	19.08	88.04	19.47	1,585.91				
OUT													
Methanator Product Gas													
Dry Gas	1,655	37,535	87	534	355.54	17.53	87.50		441.58				
Steam	361	7,601	87	534	40.11			20.06	451.61				
Condenser Duty									425.43				
Heat Loss									(267.29)				
Total	2,016				395.65	17.53	87.50	20.06	1585.91				
(Out-In) X 100	-0.93				0.00	-8.12	-0.61	+3.03					
IN													
Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
SCFH(LB/HR)													
Dry Gas	21,569	22,055	29,640	51,695	0	37,535	7,895	0					
H ₂ O	2,167	1,681	105	1,786	0	7,601	28	(355)					
Dowtherm A									(77,270)	0	(77,270)	(2,625)	(2,625)
Temperature, °F	205	645	165	556		534	534	69	548	-	563	556	479
Pressure, PSIG	114	112	150	97		87	87	87					
Composition, Mol %													
H ₂	62.12	62.95	2.80	28.46		2.80	2.80						
N ₂	4.60	4.50	8.85	6.99		8.85	8.85						
CO	14.60	12.07	0.00	5.15		0.00	0.00						
CH ₄	14.15	13.83	88.35	56.56		88.35	88.35						
CO ₂	4.55	6.65	0.00	2.84		0.00	0.00						
H ₂ O, BTU/SCF	391	382	901	680		901	901						

Table 8-3. HEAT AND MATERIAL BALANCE-RUN 33B

2/21/76 0700 HRS-2/21/76 1630 HRS
 Datum; Liquid H₂O @77°F

IN	LBS/HR	SCFH	PSIG	°F	Moles				Heat Content, MBTU				
					H	N	C	O					
Methanator Feed Gas													
Dry Gas	1,941	51,000	97	553	380.39	19.38	87.06	15.03	572.51				
Steam	91	1,919	97	553	10.13			5.06	115.68				
Heat of Reaction													
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	88,700 BTU/LB Mole								595.80				
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	71,000 BTU/LB Mole								288.26				
Total	2,032				390.52	19.38	87.06	20.09	1,572.25				
OUT													
Methanator Product Gas													
Dry Gas	1,642	37,055	87	540	350.51	17.60	86.48	0.20	447.86				
Steam	360	7,580	87	540	40.00			20.00	450.88				
Condenser Duty									434.46				
Heat Loss									(239.05)				
Total	2,002				390.51	17.60	86.48	20.20	1,572.25				
(Out-In) X 100					0.00	-9.18	-0.67	0.55					
IN													
Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
SCFH(LB/HR)													
Dry Gas	21,314	21,721	29,279	51,000	0	37,055	7,776	0					
H ₂ O	2,220	1,814	105	1,919	0	7,580	7,475	(354)					
Dowtherm A									(29,745)	0	(29,745)	(2,618)	(2,618)
Temperature, °F	207	643	172	553		540	70	70	551	-	569	560	475
Pressure, PSIG	114	112	152	97		87	87						
Composition, Mol %													
H ₂	61.83	62.54	2.55	28.10		2.55	2.55						
N ₂	4.86	4.77	9.00	7.20		9.00	9.00						
CO	13.86	11.72	0.00	4.99		0.00	0.00						
CH ₄	14.11	13.84	88.35	56.62		88.35	88.35						
CO ₂	5.35	7.12	0.10	3.09		0.10	0.10						
HIV, BTU/SCF	587	380	901	679		901	901						

Table 8-4. HEAT AND MATERIAL BALANCE-RUN 33B

9/29/77 0800 HRS

Datum: H₂O Liquid @ 77°F

IN										OUT									
Methanator Feed Gas										Methanator Product Gas									
Dry Gas										Dry Gas									
Steam										Steam									
Heat of Reaction										Heat of Reaction									
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$										$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$									
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$										$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$									
Total										Total									
549										549									
88,700 BTU/LB Mole										88,700 BTU/LB Mole									
71,000 BTU/LB Mole										71,000 BTU/LB Mole									
541										541									
-1.46										-1.46									
(Out-In) X 100										(Out-In) X 100									
IN										IN									
Stream										Stream									
1										1									
2										2									
3										3									
4										4									
5										5									
6										6									
7										7									
8										8									
9										9									
10										10									
11										11									
12										12									
13										13									
SCFH(LB/HR)										SCFH(LB/HR)									
Dry Gas										Dry Gas									
H ₂ O										H ₂ O									
Dowtherm A										Dowtherm A									
Temperature, °F										Temperature, °F									
Pressure, PSIG										Pressure, PSIG									
115										115									
Composition, Mol %										Composition, Mol %									
H ₂										H ₂									
N ₂										N ₂									
CO										CO									
CH ₄										CH ₄									
CO ₂										CO ₂									
HHV, BTU/SCF										HHV, BTU/SCF									
374										374									
796										796									
2.49										2.49									
15.31										15.31									
0.00										0.00									
78.03										78.03									
4.17										4.17									
370										370									
796										796									
2.49										2.49									
15.31										15.31									
0.00										0.00									
78.03										78.03									
4.17										4.17									
370										370									
796										796									
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15.31										15.31									
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15.31										15.31									
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370										370									
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78.03										78.03									
4.17										4.17									
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15.31										15.31									
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78.03										78.03									
4.17										4.17									
370										370									
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Table 8-5. HEAT AND MATERIAL BALANCE-RUN 47B

IN								Moles			Heat Content, MBTU	
	Methanator Feed Gas						H	N	C	O		
	Dry Gas						93.40	6.46	18.27	13.71	189.85	
	Steam						7.28		3.64		82.74	
Heat of Reaction												
	$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$											
	$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$											
Total	88,700 BTU/LB Mole 71,000 BTU/LB Mole	9.165 Moles of CO 1.276 Moles of CO					100.68	6.46	18.27	17.35	1,176.13	
OUT												
	Methanator Product Gas											
	Dry Gas						69.63	5.80	18.03	1.99	86.92	
	Steam						31.05		15.53		346.05	
Condenser Duty							100.68	5.80	18.03	17.52	401.32	
Heat Loss									-1.31	+0.98	(341.84)	
Total							100.68	5.80	18.03	17.52	1,176.13	
(Out-In) X 100												
	In											
Stream	1	2	3	4	5	6	9	10	11	12	13	
SCFH(LB/HR)												
Dry Gas	20,492	20,668	0	20,664	0	8,218	8,218					
H ₂ O	1,555	1,379	0	1,379	0	5,885	36					
Dowtherm A												
Temperature, °F	194	630		541		500	80	80				
Pressure, PSIG	114	105		104		102	102					
Composition, Mol %							(14,200)	0	(14,200)	(2,298)	(2,298)	
H ₂	60.22	60.56		60.56		3.49						
N ₂	5.97	5.92		5.92		13.37						
CO	17.81	16.81		16.81		0.00						
Cl ₄	12.65	12.54		12.54		78.54						
CO ₂	3.34	4.16		4.16		4.59						
HHV, BTU/SCF	380	377		377		805						

Table 8-6. HEAT AND MATERIAL BALANCE-RUN 47B

9/30/77 2200 iHRS
Datum: H₂O Liquid @ 77°F

IN	LBS/HR	SCFH	PSIG	°F	Moles				Heat Content, MBTU				
					H	N	C	O					
Methanator Feed Gas													
Dry Gas	2,375	55,400	82	543	398.53	34.21	98.20	19.66	607.72				
Steam	74	1,550	82	543	8.18			4.09	93.09				
Heat of Reaction													
$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	88,700 BTU/LB Mole	8.341 Moles of CO							739.85				
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	71,000 BTU/LB Mole	0.705 Moles of CO ₂							50.06				
Total	2,449				406.71	34.21	98.20	23.75	1,490.72				
OUT													
Methanator Product Gas													
Dry Gas	2,196	44,699	72	560	377.88	34.20	98.01	9.91	550.06				
Steam	260	5,463	72	560	28.83			14.41	330.05				
Condenser Duty									351.67				
Heat Loss									(258.94)				
Total	2,456				406.71	34.20	98.01	24.32	1,490.72				
(Out-In) X 100	+0.29				0.00	-.03	-.19	+2.40					
IV													
Stream	1	2	3	4	5	6	7	8	9	10	11	12	13
SCFH (LB/HR)													
Dry Gas	17,683	55,400	37,717	54,149	1,251	44,699	6,982	0					
H ₂ O	1,432	1,550	118	1,515	35	5,463	22	(253)					
Dowtherm A													
Temperature, °F	197	560	199	543	389	560	61	61	515	495	548	538	342
Pressure, PSIG	114	94	165	82	82	69	69						
Composition, Mol %									(14,600)	(3,650)	(14,600)	(1,575)	(1,575)
H ₂	61.04	21.12	2.40	21.12	21.12	2.40	2.40						
N ₂	5.73	11.70	14.50	11.70	11.70	14.50	14.50						
CO	17.89	5.71	0.00	5.71	5.71	0.00	0.00						
CH ₄	12.17	57.60	78.90	57.60	57.60	78.90	78.90						
CO ₂	3.17	3.87	4.20	3.87	3.87	4.20	4.20						
HHV, BTU/SCF	578	669	805	669	669	805	805						

(14,600) (3,650) (14,600) (1,575) (1,575)

Table 8-7. HEAT AND MATERIAL BALANCE-RUN 47B

8.3.3 DATA CALCULATION PROCEDURES

8.3.3.1 Heat and Material Balances

In performing the heat and material balance calculations which are presented in the report, the pilot plant process data were handled in the following manner: For Run 33B, all gas analyses, stream flows, etc., were averaged over the time period of interest. This was done to help smooth the data, particularly the gas composition data. All gas compositions were obtained using the laboratory gas chromatographs outlined in Section 8.6. Since each laboratory gas analysis requires approximately 15 minutes to complete, simultaneous gas analyses were not available. Additionally, the laboratory chromatograph time could not be dedicated totally to the methanation unit operation because of the need to monitor many process gas streams in the main gasification section. Therefore, the sampling time between samples of interest was often much longer than desired.

All heat and material balances presented are based upon a forced hydrogen balance to obtain the product gas rate from the packed-tube methanators. This was done because preliminary material balances indicated that the measured product rate was too large. Errors in the measured product rate were especially likely because the flow measuring orifice was sized for approximately three times the normal flow rate. This was done in anticipation of larger feed gas rates. Often the measured orifice differential pressure was less than 10 percent of the design range. Slight misalignment between the orifice differential pressure transmitter and the flow rate indicator or recorder could easily account for the high product gas rates. The measured feed gas rate, to the unit was assumed to be more reliable than the product gas rate, because the measured differential pressure across the flow orifice was normally greater than 50 percent of the design range. By forcing the hydrogen balance as described above, good carbon and oxygen balances were obtained.

Additional evidence that the product gas rate was incorrect was obtained during Run 47B. Prior to the run, a new resized product flow orifice was installed. The average percent closure in the hydrogen balance ($(\text{hydrogen out} - \text{hydrogen in}) \times 100 / (\text{hydrogen in})$) using the measured input and effluent flow rates was 2.26 percent for the three cases presented in Tables 8-5, 8-6, and 8-7. This compares with 11.5 percent for the Run 33B cases.

By the time Run 47B was conducted, on-line process chromatographs were functional in the methanation unit. Two chromatographs continuously monitored five different streams for major components (H_2 , N_2 , CO , CH_4 , and CO_2 .) A single analysis required approximately 3 minutes to perform. For Run 47B, simultaneous gas analyses for all streams of interest were available. The on-line chromatograph analyses provided a means of eliminating heat and material balance errors due to gas analysis changes caused by differences in sampling times. Therefore, the Run 47B heat and material balances were calculated for specific times with a minimal amount of data averaging. Comparisons were made between the process and laboratory gas analyses. Generally, the analyses agreed well. Since the laboratory chromatographic gas analyses were considered to be the most accurate, the process gas chromatographs readings were corrected to account for differences between the continuous process gas and laboratory chromatograph analyses. Both the laboratory and process gas chromatographs were recalibrated on a daily basis.

All gas analyses were obtained on a dry basis. However, in order to determine the actual process gas flow rates, the amount of moisture in each stream is required. Generally reasonable approximations for the moisture content could be made, assuming saturation conditions at specific points within the process. The carbonate tower feed gas was assumed to be saturated at the temperature and pressure conditions prevailing at the flow measuring orifice just upstream of the tower. The packed-tube reactor recycle and the adiabatic reactor feed gases were assumed to be saturated at the temperature and pressure conditions of the F-401 water knock-out pot. To obtain the moisture content of the carbonate tower overhead, vapor pressure curves for water over solutions of K_2CO_3 - $KHCO_3$ - H_2O were used.⁽¹⁾

One might assume that the moisture content of the ZnO effluent is the same as that of the carbonate tower overhead. However, a comparison of the carbonate tower overhead and ZnO effluent gas analyses reveals that CO shift is occurring in either the HDS furnace or in the ZnO tower. The majority of the data for all runs indicates that forward shift of the carbonate tower overhead gas to produce more hydrogen normally occurs and that the extent of the shift is somewhat variable between runs. The exact location of the shifting is not known, since no attempt was made to analyze the HDS furnace effluent. The temperatures of the HDS furnace and the ZnO effluent streams also failed to pinpoint the location, since equilibrium at the prevailing temperatures of these units was not established.

In performing the heat and material balance calculations for the methanation unit, the CO shift downstream of the carbonate tower was considered. For Run 33B, no means were available for measuring the moisture content of the ZnO effluent. The moisture content of the ZnO effluent was calculated based upon the shift equilibrium which appeared to exist at the ZnO outlet. For Run 33B, chronologically close together gas analyses for the carbonate tower overhead and the ZnO effluent streams are available. Table 8-8 presents these data and the results of calculations to determine the equilibrium shift constant. The shift constant and the moisture in the ZnO effluent were calculated based upon the change in CO concentration between the carbonate tower and ZnO effluent streams. If the data were more accurate, the measured and calculated ZnO effluent dry gas compositions should be identical. In general, the calculated composition closely approximates the measured values. Since the calculated equilibrium constants do not vary much, the assumption was made that the moisture content of the ZnO effluent could be calculated by assuming shift equilibrium at a temperature of 950°F for all Run 33B cases.

For Run 47B, a few data are available for the moisture content of the ZnO effluent. These data, when used with the effluent gas analyses, indicate an apparent shift equilibrium temperature of 1150°F for Cases 4 and 5 and 925°F for Case 6.

(1) Bocard, J. P. and Mayland, B. J., New Charts for Hot Carbonate Process, Hydrocarbon Processing and Petroleum Refiner, 1962, 41, No. 4, 128-132.

Date	2/13/76	2/15/76	RUN 33B		2/21/76
			2/16/76	2/17/76	
Time	0900	0900	0900	0900	0100
Measured Carbonate Tower Overhead Composition, Mole % (1)					
H ₂	60.50	61.8	62.8	63.1	62.0
N ₂	4.4	3.6	3.6	3.4	3.9
CO	15.3	14.7	14.3	15.5	15.2
CH ₄	13.7	14.1	14.0	13.4	13.6
CO ₂	6.1	5.8	5.3	4.7	5.3
(H ₂ O) (2)	9.5	10.1	9.5	8.7	8.3
Measured ZnO Effluent Composition, Mol % (1)					
H ₂	61.4	62.7	63.3	62.9	61.9
N ₂	4.6	3.8	4.0	3.5	4.2
CO	12.4	12.3	12.0	13.4	13.3
CH ₄	13.7	13.9	13.7	13.6	13.1
CO ₂	7.9	7.3	7.0	6.7	7.5
Calculated ZnO Effluent Concentrations (CO Balance) Mole % (1)					
H ₂	61.5	62.6	63.5	63.8	62.6
N ₂	4.3	3.5	3.5	3.3	3.8
CO	12.4	12.3	12.0	13.4	13.3
CH ₄	13.4	13.8	13.7	13.2	13.4
CO ₂	8.5	7.8	7.2	6.4	6.9
(H ₂ O)	7.15	8.1	7.6	7.1	6.7
Equilibrium K	5.45	4.46	4.64	4.01	4.48
Equilibrium Temp., °F	910	955	945	985	953
(1) Dry Basis					
(2) Water was calculated using published vapor pressure charts for H ₂ O over K ₂ CO ₃ -KHCO ₃ -H ₂ O solutions.					

Table 8-8. DETERMINATION OF SHIFT EQUILIBRIUM CONSTANT FOR ZnO EFFLUENT

8.3.3.2 Heat Loss Calculations

The heat losses for all six heat and material balance cases were calculated by difference. In order to obtain an appreciation for what the heat losses from the system should be, two special runs were made which were designed to measure the heat losses without the complication of the methanation reactions. The first run was conducted in October, 1976, after Run 39, and the second test was made following Run 47B. The tests were simple: Nitrogen was circulated by the recycle gas compressor, J-402, through the HDS furnace, B-301; then through the ZnO unit, D-305, to the packed-tube methanator DC-402, and then back to the recycle compressor. The HDS furnace was used to heat the nitrogen. Some of the heat from the hot nitrogen was transferred in DC-402 to the Dowtherm A which was circulated at a constant rate through the reactor. When the Dowtherm temperature stabilized, the heat losses from the reactor and the Dowtherm system could be easily calculated from the change in enthalpy of the nitrogen entering and leaving the reactor. The pertinent data for the heat loss runs are presented in Table 8-9.

Since less gas was circulated through DC-402 during the second test, the final Dowtherm temperature is considerably lower than for the first test. In the second test, the heat loss for the Dowtherm temperature attained is higher than expected. This is primarily due to loss and deterioration of insulation on some of the Dowtherm piping.

Since the Dowtherm temperature during normal methanator operating runs are higher than the temperatures achieved during the special heat loss tests, the special test heat losses must be corrected. This can be readily done if most of the heat loss from the system is due to conduction through the piping and reactor insulation. Because the temperature change for the Dowtherm is not great, the thermal conductivity of the insulation can be assumed to be constant. Then by using Fourier's Law for conduction (thermal conductivity, heat transfer area, and insulation thickness all constant) it can be shown that:

$$q_2 = \frac{q_1 \Delta T_2}{\Delta T_1} \quad (8-4)$$

Where: q_1 = Heat loss at base conditions (special heat loss run), Btu/hr
 q_2 = Heat loss at new conditions, Btu/hr
 ΔT_1 = Temperature drop across insulation for base case. Equal to the Dowtherm temperature minus the ambient temperature, °F.
 ΔT_2 = Temperature drop across insulation for new conditions for Dowtherm and ambient temperatures, °F.

Date	Time	Flow Rate of N ₂ to DC-402 SCFH	Gas Temperature Into DC-402 °F	Gas Temperature Leaving DC-402 °F	Temperature of Dowtherm to DC-402 °F	Ambient Temperature °F	Heat Loss MBTU/HR
<u>Special Heat Loss Run No. 1</u>							
10/15/76	1900	54,980	652	462	460	35	197.04
10/15/76	2000	55,060	655	461	460	34	201.50
10/15/76	2100	54,830	655	461	460	32	200.66
10/15/76	2200	54,830	655	461	460	34	200.66
							<u>199.97 AVG</u>
<u>Special Heat Loss Run No. 2</u>							
10/7/77	0530	29,890	643	324	331		178.72
10/7/77	0730	29,880	644	327	326	(48) *	177.55
10/7/77	0930	30,240	644	329	338		178.56
10/7/77	1130	30,680	644	330	341		180.60
							<u>178.86 AVG</u>

* Measured at 1300 HRS

Table 8-9. MEASURED HEAT LOSSES FROM DC-402 AND DOWTHERM SYSTEM

Equation 8-4 was used to predict the expected heat losses for the six heat and material balance cases. The results of the first special heat loss run were used to predict the heat losses for the Run 33B cases, while the results of the second heat loss run were used to predict the heat losses for the Run 47B cases. Because nitrogen and Dowtherm A liquid were not circulated through the single-tube reactor during the second special heat loss test, an additional correction was added to the heat loss predicted by Equation 8-4 for the sixth case. The correction, which was 57,000 Btu/hr, was determined via a heat balance around the single-tube reactor and inlet gas and Dowtherm piping.

The expected and calculated heat losses for the six heat and material balances cases are presented in Table 8-10, along with much additional information for comparing the six cases. Good agreement was obtained for the Run 33B cases, with the average absolute difference between the calculated and expected heat losses being only 17,000 Btu/hr. For the Run 47B cases, the agreement was less perfect with an average absolute difference of 76,700 Btu/hr. The poorer agreement for the Run 47B cases is most probably caused by errors in the methanator gas compositions and the Dowtherm liquid drain rates from the C-406 condenser. Errors in these data will cause significant errors in the calculated heat losses.

8.4 INTERPRETATION OF RESULTS

8.4.1 EFFLUENT GAS CO CONTENT

One of the critical SNG (substitute natural gas) specifications is that the CO content shall be less than 0.1% (1000 PPM.)

During Run 47B, special gas analyses were made to accurately determine the concentration of CO in the effluents of the DC-402 and DC-404 packed-tube reactors. This was done to determine the need for polishing reactor DC-403. During previous runs, the actual amount of CO in the packed-tube reactor effluent was unknown because the laboratory and on-line process chromatographs were not calibrated for very low CO concentrations. The measurement of the low CO concentrations was accomplished using Drager gas detector tubes CO 10/b and CO 5/c. The results of the Run 47B analyses are presented in Table 8-10. For the no-recycle gas cases shown, the effluent CO concentration (dry basis) varied between 40 and 45 PPM. For Case 6, the CO concentration from DC-402 was 250-260 PPM, while that for DC-404 was 275 PPM. All concentrations were well below the 1000 PPM specification. These results clearly demonstrate that systems consisting of only a single stage of packed-tube reactors can be designed; that secondary clean-up or polishing reactors are needed only to avoid an inadvertent CO breakthrough in the primary reactor.

Period	Case 1		Case 2		Case 3		Case 4		Case 5		Case 6	
	1800 HRS 2/17/76	0400 HRS 2/18/76	2300 HRS 2/18/76	1400 HRS 2/19/76	0700 HRS 2/21/76	1630 HRS 2/21/76	0800 HRS 9/29/77	DC-402	2200 HRS 9/24/77	DC-402	2200 HRS 9/30/77	DC-404
Reactor	DC-402	DC-402	DC-402	DC-402	DC-402	DC-402	DC-402	DC-402	DC-402	DC-402	DC-402	DC-404
Mass flux, LB/FT ² -HR (1)	1180		1192		1203		905		1135		950	572
Recycle Ratio (2)	1.42		1.25		1.25		0		0		1.97	1.97
Dowtherm Circulation Rate, LB/HR	77,400		77,300		29,700		14,300		14,200		10,950	3,650
Dowtherm Vaporized, % (3)	1.1		0.95		11		20		30		26	0
Hot Spot Temperature, °F	801		829		830		895		938		713	886
Outlet CO conc., PPM	NA		NA		NA		40		45		255	275
K eq. Shift (4)	NA		NA		NA		36.4		49.7		32.3	30.0
K eq. CO Meth., ATM ⁻² (5)	NA		NA		NA		4.1 X 10 ⁷		8.2 X 10 ⁶		9.2 X 10 ⁵	9.1 X 10 ⁵
Approach to Shift Equilibrium Temp, °F (6)	NA		NA		NA		67		-2 to -10		23 to 38	-9
Approach to CO Methanation Equilibrium temp, °F (6)	NA		NA		NA		38		35 to 43		68 to 83	24
Measured overall U, BTU/HR-FT ² -°F (7)	51		34		33		23		31.5		58	-
Average Predicted Inside Film Coefficient, BTU/HR-FT ² -°F (8)	131		125		124		53		64		115	60
Average Predicted Outside Film Coefficient, BTU/HR-FT ² -°F	8.4		8.2		3.8		1.7		1.7		1.4	34
Calculated overall U, BTU/HR-FT ² -°F	7.85		7.65		3.68		1.65		1.65		1.38	21
Measured Heat Flux (Q/A), BTU/HR-FT ²	7,150		5,560		5,060		4,260		5,100		2,790	3,560
Calculated Heat Loss, MBTU/HR	265		267		239		199		342		259	
Expected Heat Loss, MBTU/HR	242		242		242		289		289		346	
(1) Based upon fresh feed only-recycle not included.												
(2) Ratio of recycle gas (wet) to fresh feed (wet).												
(3) Assumed no heat loss from reactor.												
(4) Equilibrium shift constant based upon measured effluent gas composition from reactor.												
(5) CO methanation equilibrium constant based upon measured effluent gas composition from reactor.												
(6) Difference between equilibrium temperature (shift or CO Methanation) and measured temperature at bottom of reactor tubes.												
(7) From point at which reaction appears to commence to hot spot peak temperature.												
(8) Based upon outside surface area.												

Table 8-10. OPERATION SUMMARY-RUNS 33B AND 47B

8.4.2 APPROACH TO EQUILIBRIUM

Once the packed-tube reactor effluent CO concentrations were known, the approach to CO shift and CO methanation equilibrium could be calculated. Table 8-10 presents these calculated shift and methanation equilibrium constants. The approach to equilibrium was determined by taking the difference between the equilibrium temperature for the calculated equilibrium constants and the temperature which existed at the outlets of the catalyst filled tubes. There is scatter in the meager amount of data that was obtained for Run 47B. This is particularly evident when the CO shift equilibrium approach temperatures are considered. The negative approach temperatures are not realistic, since one would expect a positive value. Again, slight errors in the measured gas concentration, particularly for hydrogen or carbon dioxide, would easily account for the negative values and the scatter in approach temperatures. An average of the available data indicates a shift equilibrium approach of about 20°F and a CO methanation equilibrium approach of about 50°F.

8.4.3 CATALYST DEACTIVATION

The methanation unit was operated for 50 hours during Run 29B and for 212 continuous hours during Run 33B. During these periods, the reactor temperature profiles remained stable. Following Run 33B, DC-402 was repacked with catalyst because a valve switching operation in the methanation unit had caused a back flow of gas which blew catalyst out of some of the tubes. During the next 659 hours of methanation operation, evident catalyst deactivation was occurring. This is apparent when Figures 8-6 and 8-7 are compared. Figure 8-6 shows the temperature profiles measured in the DC-402 reactor during Run 33B. The catalyst temperature begins to rise rapidly almost as soon as the gas enters the top of the catalyst bed. The peak temperature is achieved at about 1-1/4 feet below the top of the catalyst bed. Similar temperature profiles for the Run 47B heat and material balances are presented in Figure 8-7. This figure shows that the temperature peak has migrated approximately 2 feet further down the tube and that considerable spreading or broadening of the temperature profile has occurred.

To determine the cause of the catalyst deactivation, samples of the catalyst from specific tubes in DC-402 and from DC-404 were sent to the manufacturer, Katalco Corporation, and to the licensor, British Gas Corporation, for analysis. The samples were analyzed for sulfur, carbon, and potassium. Sulfur is a well-known poison for methanation catalyst, so its presence would be the most likely cause of the catalyst deactivation. The presence of carbon could indicate carbon lay-down and plugging of the catalyst pores. The potassium analysis was to determine if carryover of carbonate tower mist had occurred.

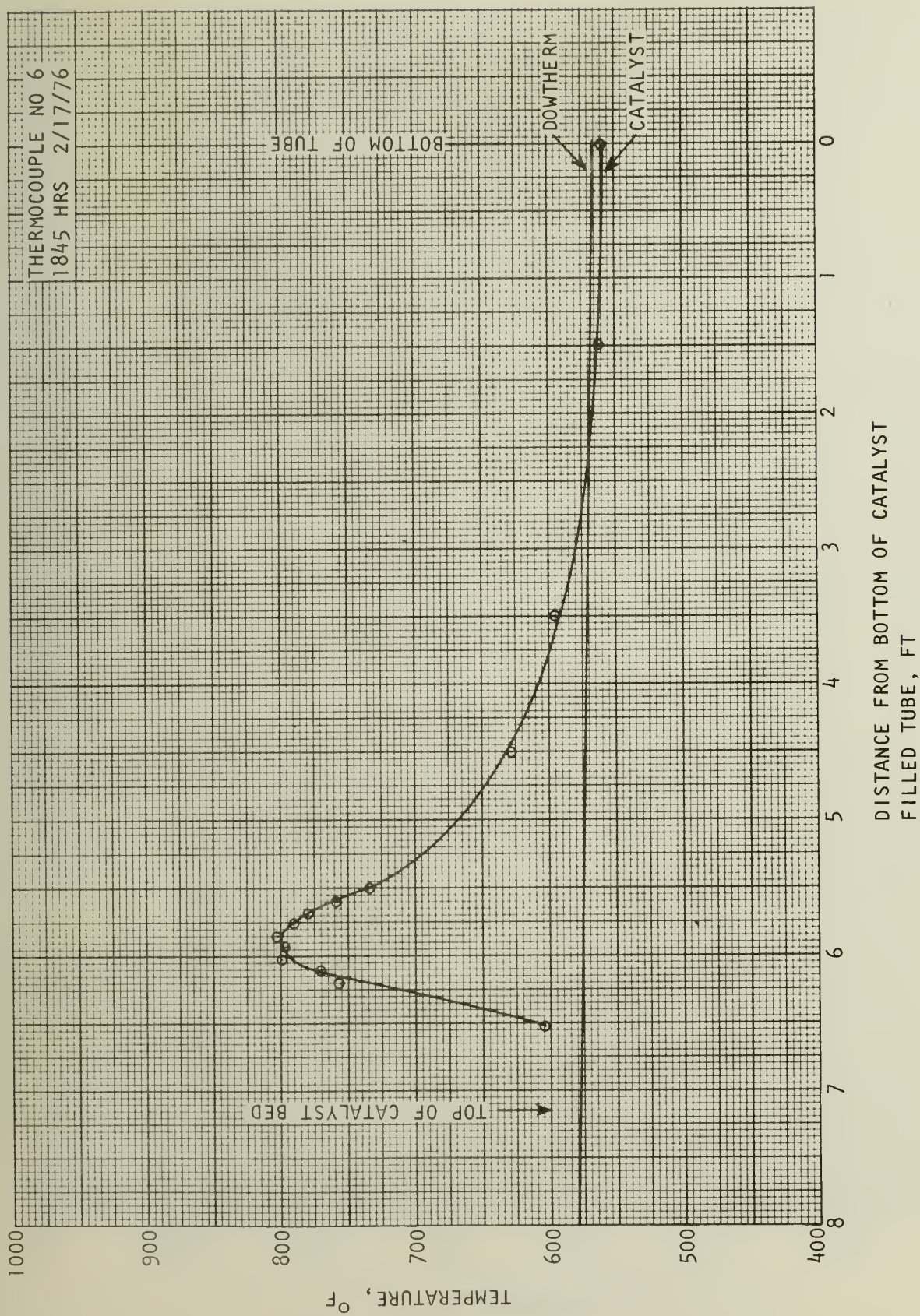


Figure 8-6. DC-402 REACTOR TEMPERATURE PROFILES, RUN 33B (Sheet 1 of 3)

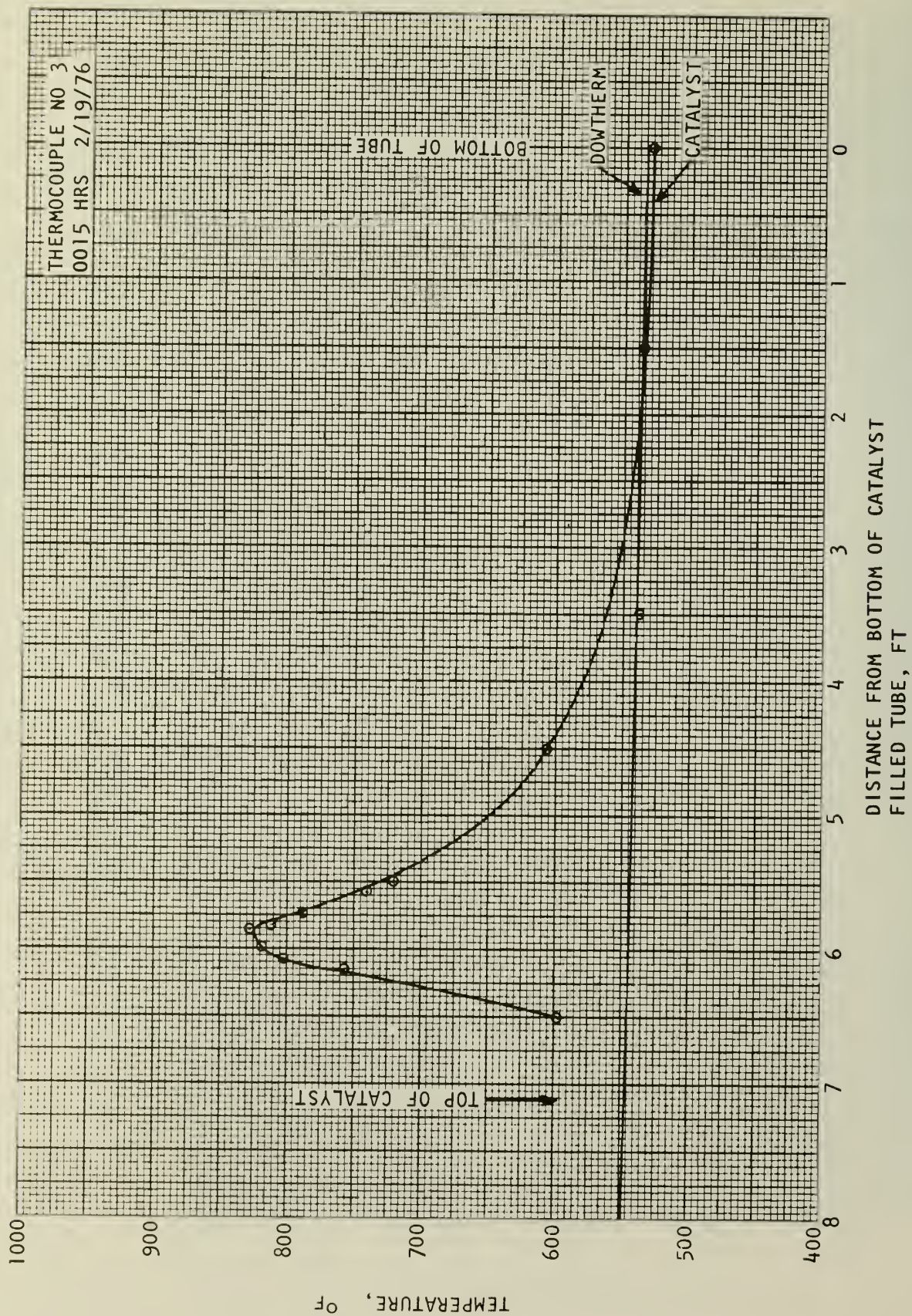


Figure 8-6. DC-402 REACTOR TEMPERATURE PROFILES, RUN 33B (Sheet 2 of 3)

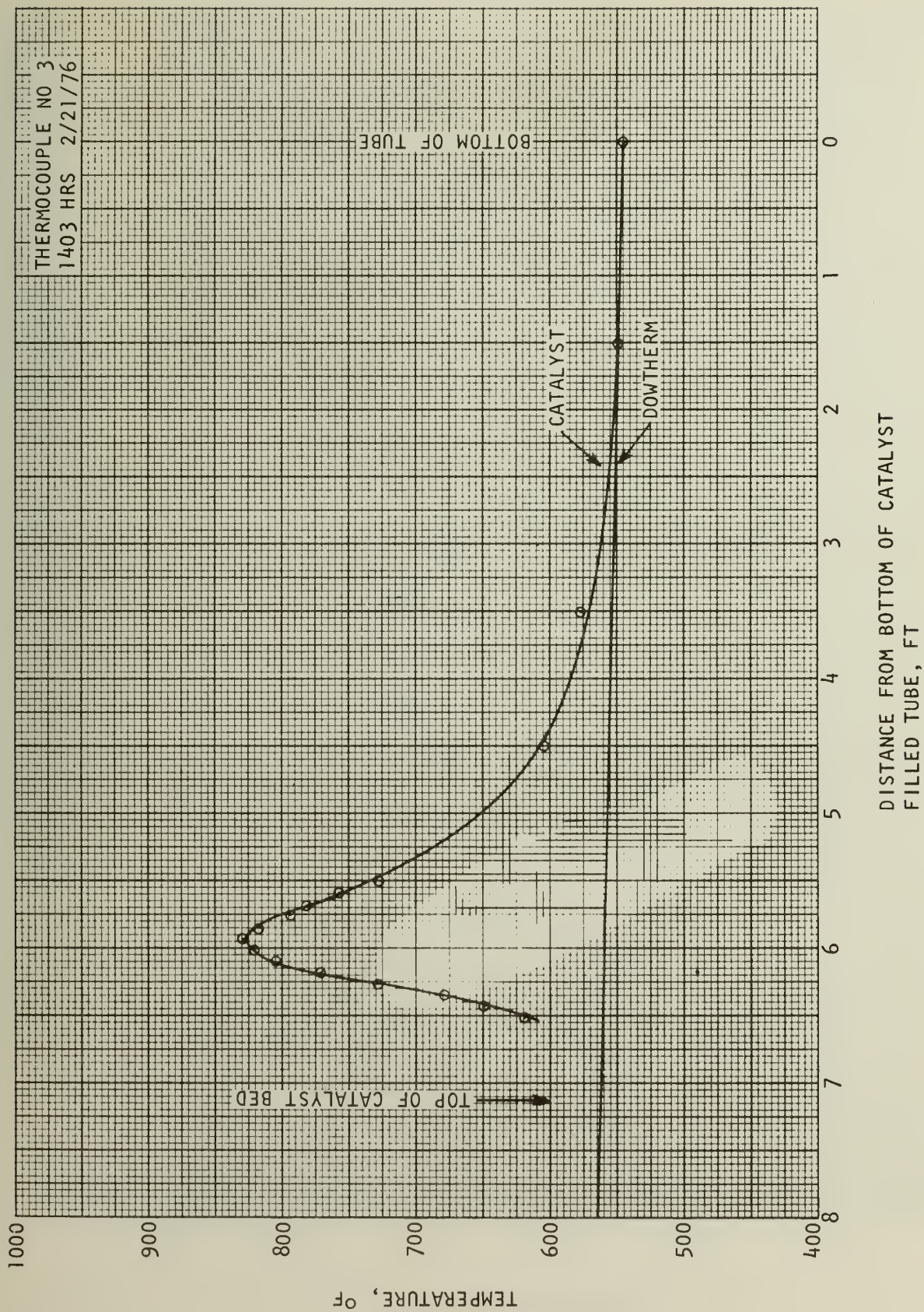


Figure 8-6. DC-402 REACTOR TEMPERATURE PROFILES, RUN 33B (Sheet 3 of 3)

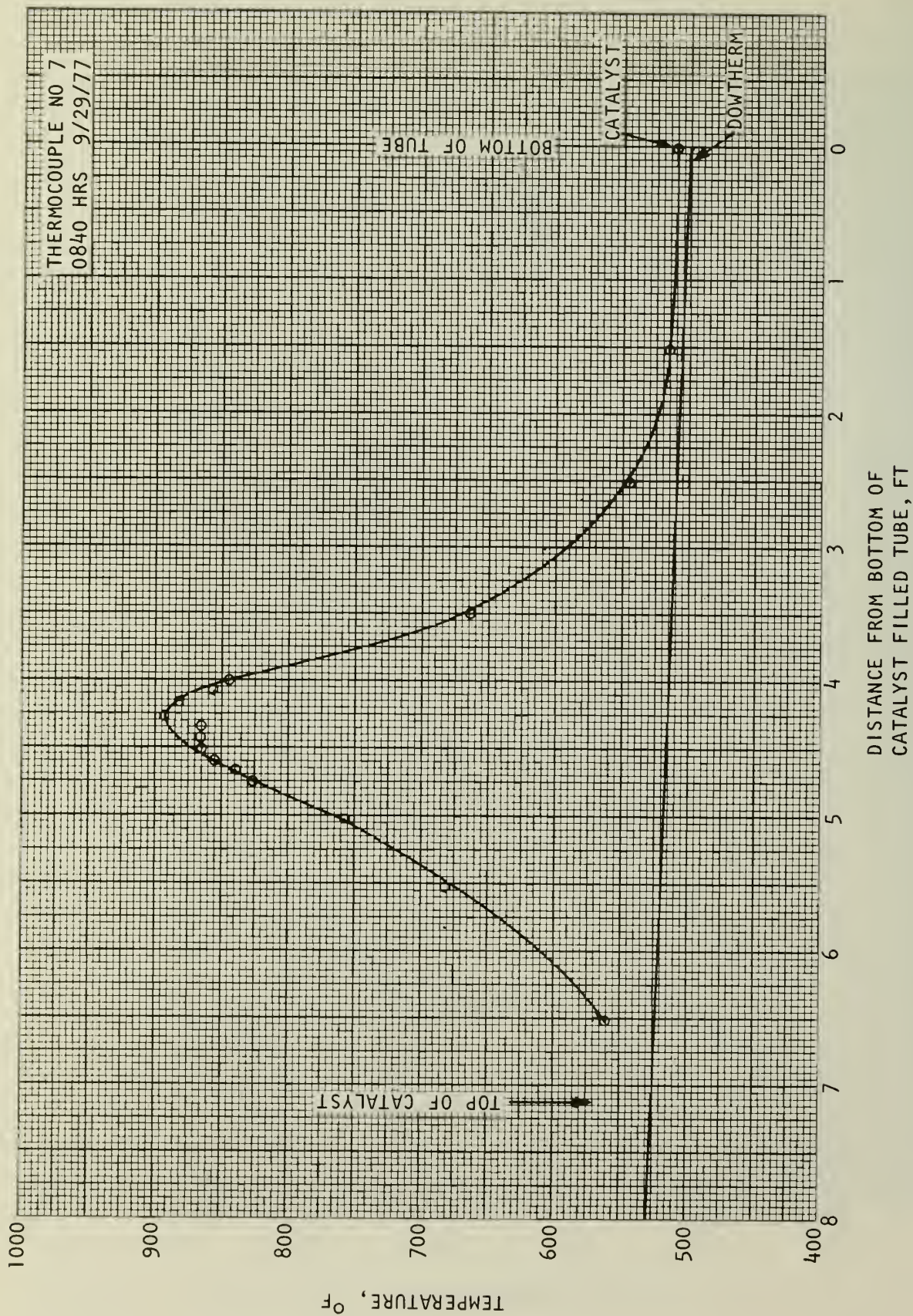


Figure 8-7. DC-402 AND DC-404 REACTOR TEMPERATURE PROFILES, RUN 47B (Sheet 1 of 3)

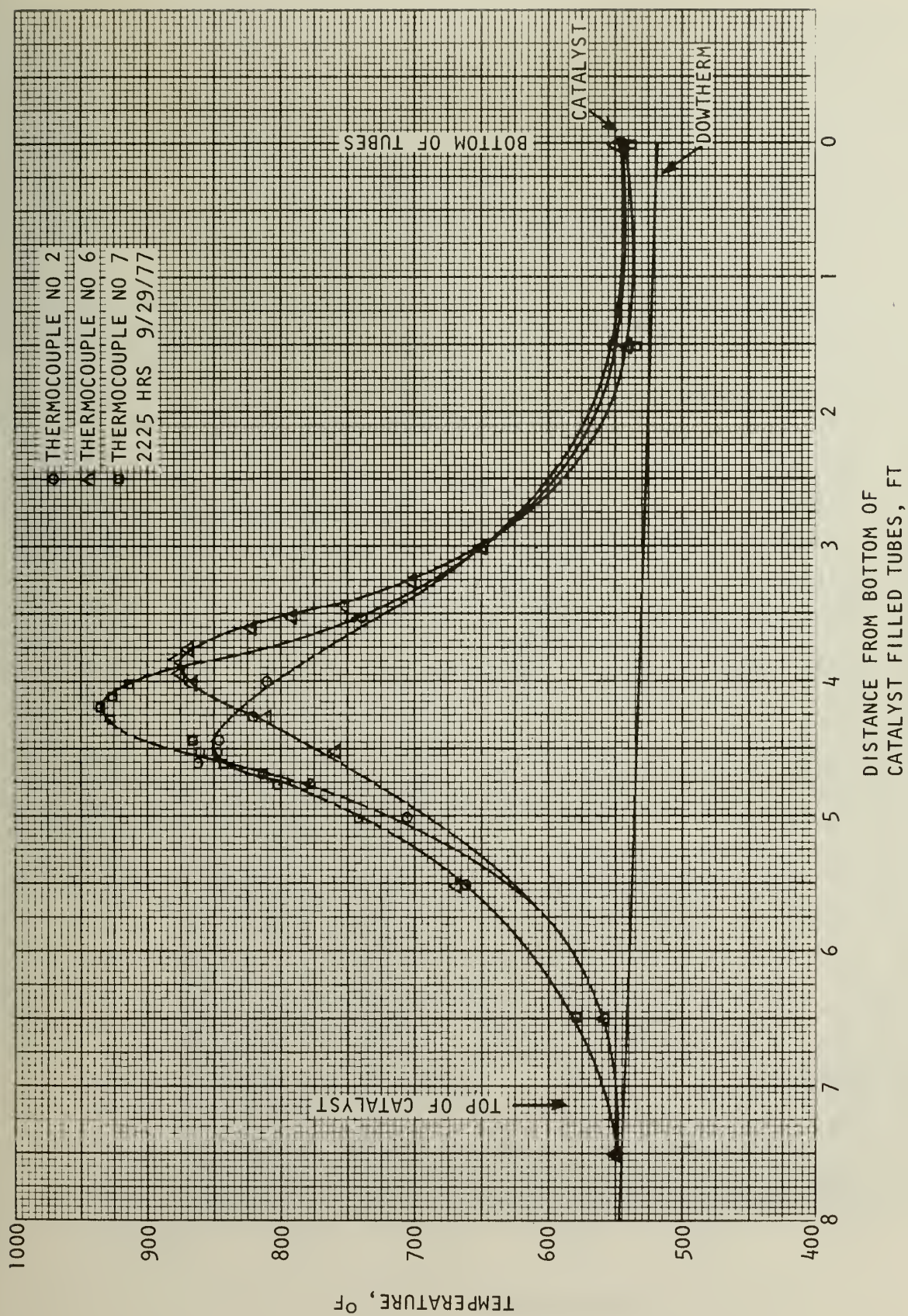


Figure 8-7. DC-402 AND DC-404 REACTOR TEMPERATURE PROFILES, RUN 47B (Sheet 2 of 3)

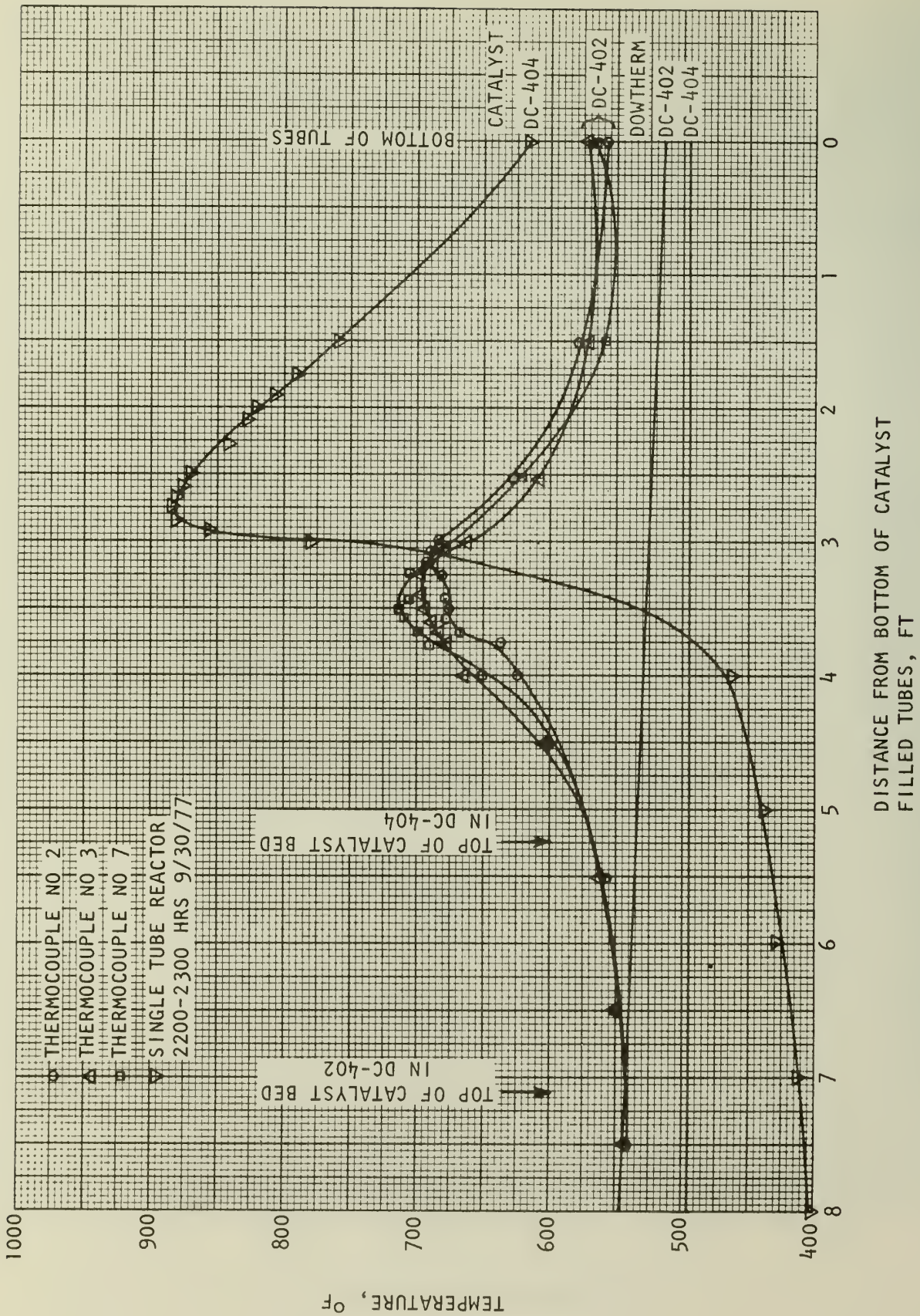


Figure 8-7. DC-402 AND DC-404 REACTOR TEMPERATURE PROFILES, RUN 47B (Sheet 3 of 3)

The British Gas analyses confirm Katalco's analyses which are presented in Table 8-11. A slight carbon profile exists in both the DC-402 and DC-404 catalyst beds. The top of the catalyst bed contains from 0.4 to 0.9 wt percent more carbon than the bottom of the bed. It is not known if any carbon was deposited on the bottom bed samples, since a sample of the fresh reduced catalyst was not available. However, the amount of carbon deposited may have reached a stable level. This is indicated, since the amount of carbon in the single tube reactor catalyst, which had been operated for only 135 hours, was essentially identical to that found in samples from the packed-tube methanator, DC-402, which had been in operation for 659 hours.

The potassium analyses show only a slight concentration increase towards the top of the catalyst bed for the DC-402 samples. A much greater potassium concentration gradient is shown for the single-tube reactor samples. The reason for the larger amount of potassium in the DC-404 catalyst samples is not readily apparent. However, some minor amount of carbonate mist carryover into the methanation reactors is indicated.

The sulfur analyses definitely show a large sulfur concentration gradient throughout the catalyst beds for both reactors. In the single-tube reactor, the top 19% of the catalyst bed contained four times the sulfur concentration of the bottom 30%; while in the DC-402 reactor the top 25% of one tube sample contained 17 times the amount of sulfur contained in the bottom 30% of the catalyst bed. Sulfur poisoning clearly is responsible for the methanation catalyst deactivation. Channeling of synthesis gas through the ZnO sulfur guard bed or the leakage of synthesis gas through block valves around the ZnO unit is probably responsible for the poisoning.

With a highly active catalyst, such as that for Run 33B, the rate of methanation is so rapid that steep temperature profiles are obtained. Most of the methanation reaction takes place in a small volume of catalyst. This results in the need to transfer a large amount of reaction heat through a relatively small heat transfer area. Attempts to operate without gas recycle would have resulted in peak temperatures well in excess of 950° F. Such high temperatures are to be avoided because they promote nickel crystallite growth which results in catalyst deactivation.

The partial sulfur poisoning of the catalyst was beneficial, in that it allowed methanator operation without the need to supply recycle gas for temperature control. The less active catalyst at the top of the reactor produced a lower rate of reaction, which allowed the temperature profile in a tube to broaden. More surface area for heat transfer was available, so peak temperatures could be controlled without gas recycle. Table 8-10 presents two cases (Cases 4 and 5) for which no recycle gas was required. The cases differ primarily in the mass flux of fresh feed gas to the reactor, with Case 5 having a 1.25 times greater flux rate than Case 4.

Samples	Catalyst Fraction*	Weight Percent of Sample		
		Carbon	Potassium	Sulfur
Packed-tube	29.6	-	0.18	0.05
Methanator, DC-402	29.6	4.1	0.19	0.36
	25.2	-	0.19	0.67
	15.7	4.7	0.22	0.66
Packed-tube	29.9	3.8	0.17	0.04
Methanator, DC-402	22.4	-	0.19	0.19
	22.2	4.2	0.19	0.60
	25.5	-	0.20	0.68
Single-tube	30.3	3.7	0.17	0.04
Methanator, DC-404	30.5	4.1	0.20	0.06
	20.1	4.4	0.39	0.11
	19.2	4.6	0.92	0.16

*Fraction of catalyst in tube from bottom to top of catalyst bed.

Table 8-11. ANALYSES OF CATALYST REMOVED FROM REACTORS, DC-402
AND DC-404 AFTER RUN 47B

Originally, it was intended to simulate the methanator operation by developing a computer program to account for the heat transfer and the kinetics in the reactor. Since there were no kinetic expressions in the public domain specific for the CRG-A catalyst, modification of existing literature kinetics expressions for other nickel methanation catalysts would have been attempted. A comparison of the measured temperature profiles in the catalyst-filled tubes with the predicted profiles from the model would have substantiated the kinetic expressions used.

Sulfur poisoning of the catalyst has created varying levels of catalyst activity throughout the catalyst bed. This is indicated by the temperature profiles for Cases 4 and 5, which show that the catalyst at the top of the bed still retains some activity. Under these conditions, modeling of the reactor becomes far more difficult and attempts to establish reaction models were therefore abandoned.

8.4.4 REACTOR HEAT TRANSFER

The design of a commercial packed-tube reactor requires a knowledge of heat transfer rates between the catalyst and coolant. The data from the Rapid City operations are too limited to provide adequate design information. Nonetheless, orienting data have been derived from the operation of reactors DC-402 and DC-404.

It is estimated, for the six cases presented in Table 8-9, that between 70 and 90% of the total heat released by the methanation reaction is generated in the volume of catalyst between the top of the catalyst bed and the location of the hot spot. Since the actual catalyst volume may have been reduced from the original volume due to settling, and to avoid considering the heat transfer area associated with totally deactivated catalyst, the volume of catalyst considered in determining the heat transfer coefficients is that volume between the point at which the catalyst temperature begins to rise and the location of the hot spot peak. For the single-tube reactor operation shown in Case 6, the volume of catalyst considered was between the point at which the catalyst temperature equalled the Dowtherm A temperature and the hot spot. This zone was chosen because the synthesis gas entered the reactor below the Dowtherm A temperature due to heat losses from the gas lines leading to the reactor.

To determine the overall heat transfer coefficients and heat fluxes in the selected zones, the amount of reaction must be known. Gas compositions were not attainable from the reactor at the location of the peak temperature. The gas composition at the peak temperature was calculated from equilibrium relationships assuming equilibrium approach temperatures of 20° F for CO shift and 50° F for CO methanation. Once the composition at the peak temperature is determined, a heat and material balance around the selected zone can be made to determine the amount of heat (Q) transferred to the Dowtherm. The assumption is made that there is a negligible radial temperature gradient at all points along the tube length.

In the reactor, the amount of heat transferred through the differential area dA is:

$$dQ = U dA \Delta T \quad (8-5)$$

Where: dQ = The differential heat flow, Btu/hr
 U = The overall heat transfer coefficient, Btu/(hr) (ft²) (°F)
 dA = The differential heat transfer area based upon the outside area of the tube or tubes, ft²
 ΔT = The difference between the catalyst temperature and the Dowtherm A temperature, °F.

The reactor differential heat transfer area is:

$$dA = n \pi D_o dL \quad (8-6)$$

Where: n = Number of catalyst-filled tubes
 D_o = Tube outside diameter, ft
 dL = Differential length of tube, ft

Then U is determined by:

$$U = \frac{\int_0^Q dQ}{n \pi D_o \int_0^L \Delta T dL} \quad (8-7)$$

Where: L = The total length of the heat transfer zone, ft.

Using the measured temperature profiles (Figure 8-6 or 8-7), plots of ΔT versus dL were made and graphically integrated to obtain the value of the integral in the denominator of Equation 8-7. The equation was then solved to obtain U . The results (measured U) are presented in Table 8-9 along with the heat flux which is defined as Q/A . The measured overall heat transfer coefficients for the packed-tube reactor, DC-402, varied between 23-58 Btu/(hr) (ft²) (°F).

For comparison with the measured overall heat transfer coefficients, overall heat transfer coefficients were calculated using empirical correlations for the inside and outside film coefficients by the following formula:

$$U = \frac{1}{\frac{1}{h_i D_i} + \frac{1}{h_o} + \frac{X_w D_o}{K_m D_L}} \quad (8-8)$$

Where: D_i, D_o = Inside and outside tube diameters, respectively, ft
 D_L = Log mean diameter, ft
 h_i, h_o = Inside and outside film coefficients, respectively, Btu/(hr) (ft²) (°F)
 K_m = Tube metal thermal conductivity, Btu/(hr) (ft²) (°F/ft)
 X_w = Tube wall thickness, ft

Fouling factors were assumed to be zero, since the reactor had only been in service for a relatively short time.

The outside film coefficient was determined using the standard Sieder and Tate correlation⁽²⁾, since neither reactor shell contained baffles. The inside film coefficient was determined using the following correlation developed by Leva, et al.⁽³⁾ for wall-to-wall cooling heat transfer in fixed beds:

$$h_i = 3.50 \frac{K_f}{D_i} e^{-4.6 D_p/D_i} \frac{(D_p V \rho_f)^{0.7}}{\mu_f} \quad (8-9)$$

Where: D_p , D_i = Particle diameter and tube inside diameter, respectively, ft
 K_f = Fluid thermal conductivity, Btu/(hr)(ft²)(°F/ft)
 V = Superficial fluid velocity, ft/hr
 ρ_f = Fluid density, lb/ft³
 μ_f = Fluid viscosity, lb/(ft)(hr)

Table 8-10 presents the calculated values for the inside film coefficient corrected to the outside tube area ($h_{i,i} \frac{D_o}{D_i}$), the outside film coefficient,

and the overall heat transfer coefficient. The calculated film coefficients show that heat transfer would be limited by the outside film resistance if the heat transfer was by convection only. A comparison of the measured and calculated overall heat transfer coefficients for the DC-402 reactor shows the measured U to be 4.4 to 9.0 times greater than the calculated U for Cases 1, 2, and 3, and 14 to 42 times greater for Cases 4, 5, and 6. Therefore, convective heat transfer alone is not sufficient to account for the actual heat transfer. Some form of nucleate boiling must have occurred on the tube surface to account for the measured rate of heat transfer.

Additional evidence that boiling was indeed occurring on the tube surface was obtained by performing heat balances around DC-402 only. Table 8-10 presents the results of these calculations which show the amount of vapor generated in the reactor. The heat balances show that substantial vaporization occurred in the reactor for Cases 3, 4, 5, and 6. For Cases 1 and 2, the percent vaporization of the entering Dowtherm flow was lower than the expected 4.7-4.8 wt. %. The Dowtherm circulation rates were much higher for the first two cases than for the last four cases. Therefore, slight errors in the Dowtherm inlet temperatures to the reactor probably account for the low calculated vaporization percentages.

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- (2) Sieder, E. N. and Tate, G. E., Heat Transfer and Pressure Drop of Liquids in Tubes, Industrial and Engineering Chemistry, 1936, 28, 1429-1435.
 (3) Leva, et al., Cooling of Gases Through Packed Tubes, Industrial and Engineering Chemistry, 1948, 40, 747-752.

To allow direct comparisons between the heat transfer in DC-402 and DC-404, attempts were made to have identical Dowtherm velocities through the shell side of the reactors. Because of heat losses from the Dowtherm inlet piping to DC-404, however, the Dowtherm circulation rate to the reactor had to be substantially increased just to maintain an inlet temperature of 489°F--which was 20°F cooler than the Dowtherm temperature to DC-402. The Dowtherm entering DC-404 was sufficiently subcooled so that no Dowtherm vaporization occurred in the reactor. However, because the Dowtherm velocity through the DC-404 shell was approximately 36 times that through the DC-402 shell, the convective overall heat transfer coefficient calculated by Equation 8-8 was about the same as the lowest measured overall coefficient for the DC-402 reactor.

As will be explained in the next paragraph, a reasonable heat release in the single-tube reactor would not be obtained based upon the gas composition change between the inlet to the reactor and the composition at the peak temperature. Therefore, the overall heat transfer coefficient could not be determined. However, what appears to be a reasonable approximation for the heat flux, in the zone between the point at which the catalyst temperature equals the Dowtherm temperature and the peak temperature (see Figure 8-7) was obtained. Equation 8-7 was rearranged

$$\int_0^Q dQ = Un\pi \int_0^L \Delta T dL \quad (8-10)$$

and the value of the left-hand integral determined by setting U equal to the value of the convective overall heat transfer coefficient and using the measured temperature profile to determine the value of the right-hand integral. The use of the convective heat transfer coefficient was justified, since boiling in the reactor does not appear to have taken place.

For the single-tube reactor case, the calculated heat release in the zone between the top of the catalyst bed and the peak temperature is not sufficient to heat the products of reaction to the measured peak temperature. Even if equilibrium conditions are assumed to exist at the peak temperature, there is not a sufficient heat release. This means that the inlet gas compositions to both DC-402 and DC-404 are somewhat in error, and that more reaction is taking place in the reactors than the change between the measured inlet and outlet gas compositions indicate. The much lower than expected heat loss (determined by difference) from the system also supports this position. It is regrettable that for Case 6 the inlet gas analysis data are not as reliable as one would desire. However, some tentative conclusions can be drawn from the results of the Case 6 operation.

The use of large-diameter tubes in the packed-tube methanation reactors is desirable to minimize construction cost and to reduce the labor cost involved in filling the reactor with fresh catalyst and in dumping spent catalyst. Based upon the pilot plant experience, however, the use of 2-inch diameter tubes over 1-inch diameter tubes is of questionable or marginal value. A comparison of the DC-402 and DC-404 temperature profiles for Case 6 clearly shows that the 1-inch diameter tubes were superior to the 2-inch diameter tubes in limiting the temperature rise in the reactor. Additionally, the mass flux of synthesis gas through DC-402 was 1.66 times the flux through the single-tube reactor. A considerably higher ratio than this would have been obtained had the gas flow rate to DC-402 been increased sufficiently to achieve the same peak temperature as in the single-tube reactor. High mass flux rates are desirable to minimize the number of tubes in a reactor and the overall diameter of a reactor.

The Case 6 results are not surprising, since the 1-inch diameter tubes have approximately 2.6 times the surface area per unit catalyst volume of that for the 2-inch diameter tubes. In addition, the hottest temperature radially across a tube occurs at the tube center. Increasing the tube diameter increases the distance heat must travel to the tube wall and, therefore, the difficulty of heat removal. The achievement of comparable temperature profiles and mass fluxes using 2-inch diameter tubes would require the use of catalysts with much lower activities than those that can be used with reactors containing 1-inch diameter tubes. The penalty for this would be a reduction in allowable space velocities and probable increased reactor pressure drop for reactor designs using 2-inch diameter tubes.

8.5 CONCLUSIONS

The majority of methanation schemes consist of various arrangements of adiabatic reactors which use gas recycle to limit the catalyst bed temperature to 900°F or less. The packed-tube methanator design provides a method of limiting the catalyst temperature through internal heat removal. The main advantage of the more complicated packed-tube reactor design over a conventional adiabatic reactor is that the compression costs for recycle can be minimized or eliminated.

Operation of the pilot plant packed-tube reactor has clearly demonstrated that "once-through" methanation without recycle can be achieved using 1-inch diameter catalyst-filled tubes, and that CO conversions which meet pipeline gas specifications can be achieved in a single reactor. However, based upon the comparison between an adiabatic reactor system and a packed-tube reactor system presented in the CO₂ Acceptor Process Commercial Plant Conceptual Design and Cost Estimate,⁽⁴⁾ the packed-tube reactor design is not economically competitive. As new methanation catalysts are developed which can tolerate higher operating temperatures, the packed-tube reactor designs will become even less attractive.

(4) Commercial Plant Conceptual Design and Cost Estimate-CO₂
Acceptor Process Gasification Pilot Plant: Period August, 1976-December, 1977
Issued: DOE Final Report No. FE/1734-43, Volume 10, Book 2
Contractor: Conoco Coal Development Company-Contract EX-76-C-01-1734
Available From: NTIS

8.6 DETAILS OF START-UP PROCEDURE & SAMPLING PRACTICES

8.6.1 START-UP PROCEDURE

Before the methanation unit was commissioned for service, a detailed start-up procedure was written. This document contained a description of the shift conversion, gas purification, and methanation sections, a general discussion of the pilot plant program objectives, equipment and instrumentation lists, possible emergency situations, and a shutdown procedure. All methanation unit operators were required to be familiar with the detailed start-up procedure. For operator convenience, the heart of the detailed procedure was incorporated into a second operating procedure which eliminated much of the process descriptive information and the operating procedure for nonused equipment. This abbreviated start-up procedure was generally followed during each startup of the methanation unit. Once the unit was operating smoothly, desired changes in the unit operating conditions were then made. A copy of the abbreviated start-up procedure is included as an Exhibit in Book 4, Subsection 13.2.1.7.

The following four sections in the methanation unit, hot potassium carbonate unit (HPC), desulfurization unit, Dowtherm unit, and the methanation reactors were brought on-line in the following manner. Although the shift conversion section was never required for the adjustment of the hydrogen-to-carbon monoxide ratio of the quenched synthesis gas, the shift conversion unit and the hot potassium carbonate tower were first purged with inert gas to displace any oxygen that might have leaked into the system. When the oxygen level was 2 volume percent or less, the shift and HPC units were pressurized with inert gas to a level which matched the pressure of gasifier synthesis gas vent header (usually about 130 psi). Synthesis gas was then admitted to the HPC tower, E-303, and vented to the flare header through a back-pressure control valve, PCV-3108, just downstream of the carbonate tower. The carbonate tower operating conditions (flow rate of lean carbonate to the tower, split of carbonate to the upper and lower beds, and the carbonate temperature) were adjusted to give the desired removal of CO_2 from the synthesis gas.

As the HPC system was put on-line, a mixture of nitrogen and about 1 volume percent hydrogen was circulated through the desulfurization system and the methanation unit reactors. Special start-up piping was included in the design to allow this. The recycle gas compressor, J-402, was used to circulate the gas mixture through the HDS furnace, B-301, to the ZnO sulfur guard, D-305, then to both methanation reactors, DC-402 and DC-403. The compressor took suction from both water knock-out pots, F-401 and F-402, which were downstream of DC-402 and DC-403, respectively. Circulation of the nitrogen-hydrogen mixture allowed the ZnO unit and methanation reactors to be heated to operating temperature by the HDS furnace.

At all times (even when the unit was shut down), a nitrogen-hydrogen gas blanket was maintained on the methanation catalyst. This was done as a precaution against any oxidation of the catalyst by air leakage into the system.

Additional heat was supplied to the methanation unit during start-up by the Dowtherm system. The Dowtherm vaporizer was operated in a manner which allowed the heating of the Dowtherm liquid in the expansion tank and the production of Dowtherm vapors. The vapors were used to preheat the inlet gases to the methanation reactors and the hot Dowtherm liquid was circulated to DC-402.

When sufficient Dowtherm vapors were generated to maintain the inlet gas temperature to the methanation reactors at 400°F or above, the methanation reactor system was separated from the desulfurization section. The nitrogen-hydrogen gas mixture was then circulated sequentially through DC-402 and DC-403 by the recycle compressor. Synthesis gas from the HPC tower was then passed through B-301 and D-305 and vented through a second back-pressure control valve, PCV-3114, into the flare header. When the sulfur level at the ZnO unit outlet was below 0.2 PPM, the desulfurization and methanation reactor systems were again tied together. Initially, the gas circulated through the methanation reactor was almost totally recycle gas. Gradually the pressure downstream of the adiabatic reactor was lowered so that more desulfurized synthesis gas would be pulled through the methanation reactors. The recycle-to-feed gas ratio gradually decreased because of the increase in feed gas flow through the methanation reactors. The heat load on the reactors increased rapidly due to the heat released by the methanation reactions, especially in the packed-tube methanator, DC-402.

When approximately 10,000 SCFH of fresh feed gas was being drawn through the methanation reactors, sufficient product gas was vented from the adiabatic reactor to maintain the reactor inlet temperature via the Dowtherm preheater, C-412. Recycle through DC-403 was then discontinued.

As the fresh feed gas rate was increased to DC-402, temperatures within the catalyst-filled tubes were monitored to ensure that the peak temperature did not exceed the desired limit (usually 850-950°F.) The temperatures were monitored through the use of thermocouples which are moved through axial thermowells in specially equipped reactor tubes.

The heat released by the methanation reactions in DC-402 caused some of the Dowtherm which is circulated through the shell side of the reactors to vaporize. Eventually, sufficient heat was absorbed by the circulating Dowtherm to cause the pressure in the Dowtherm Expansion Tank, F-407, to rise. The circulation of Dowtherm liquid to the vaporizer was then discontinued by blocking the vaporizer from the expansion tank. The vaporizer was then used only to supply vapor to the methanator feed gas preheaters, C-402 and C-412. To maintain the temperature and pressure in the Dowtherm Expansion tank, the Dowtherm vaporized in DC-402 was condensed in the air-cooled condenser, C-406. The drain rate of Dowtherm liquid from the condenser was used to measure the amount of heat absorbed by the Dowtherm in reactor DC-402.

When C-406 was operating in a stable manner, the unit was fully on-line. From these base-line sets of conditions, adjustments were then made to test the effects of various process variables on the methanation unit operations.

8.6.2 METHANATION SAMPLING

8.6.2.1 Methanation Analyses

Gas samples from the methanation section of the CO₂ acceptor process were analyzed by the laboratory in order to collect operating data and maintain process control. Results of the analyses were given to the process engineer for process flow determinations and analysis, and to the operator of the methanator to help maintain process conditions and to allow comparisons with on-line chromatograph readings.

Samples were collected by two methods: The majority of the samples analyzed were obtained from four gas sample lines which flowed gas continuously from the methanation unit to the laboratory. The sample lines were:

- (1) Carbonate tower overhead.
- (2) ZnO effluent.
- (3) Packed-tube reactor effluent.
- (4) Adiabatic reactor effluent.

The second collection method, which was practiced infrequently, was the manual collection of a sample into a bag at a sample point in the methanation unit.

The gas samples were analyzed by gas chromatography, using a Varian Model 90 gas chromatograph coupled to a Hewlett Packard 3380A integrator. A molecular sieve (13A) or a silica gel column was used for gas separation. From this analysis, the percent of hydrogen, nitrogen, carbon monoxide, carbon dioxide, and methane was reported. The chromatograph was calibrated with standard gas mixtures obtained from Air Products and Chemicals and from Linde Division of Union Carbide Corporation.

The sulfur gases in the methanation gas samples were determined by gas chromatography, with a Varian Model 1400 gas chromatograph equipped with a flame photometric detector specific for sulfur and a deactigel column for gas separation. This chromatograph was coupled to a Hewlett Packard 3380A integrator and calibrated by means of a permeation tube dilution instrument and a dilution flask.

A gas sample downstream from the CO₂ absorber was analyzed every 8 hours for major constituents, the main purpose being to control the percent of carbon dioxide going to the packed-tube methanator. A gas sample downstream from the zinc oxide tower was checked every 4 hours for major components and for sulfur gases, since even minute traces of sulfur will deactivate the methanation catalyst. Gas samples downstream of the packed-tube methanator and downstream from the adiabatic methanator were analyzed every 4 hours for their major constituents, to determine reactor performance and optimum process conditions.

8.6.2.2 Process Chromatographs

Four on-line gas chromatographs (AR-4000, AR-4001, AR-4002, and AR-4003) were installed in the methanation unit to allow continuous monitoring of the process streams. Two chromatographs, AR-4000 and AR-4001, were used to monitor process streams for major components (H_2 , N_2 , CO, CH_4 , and CO_2 .) The other two analyzers were to monitor for total sulfur. The purpose of the instrumentation was to:

- (1) Provide continuous monitoring of the process stream, thus allowing the gathering of useful material balance information.
- (2) Provide a means of monitoring transient conditions.
- (3) Reduce the operator-to-system response time.
- (4) Allow the gathering of useful data even during runs of short duration.

Although the installation of the unit was completed in November of 1976, the units (AR-4000 and 4001) were not considered to be reliable until Run 46C (July, 1977.) Many modifications to the sampling systems and to the analyzer electronics were required before useful data were obtained. Analyzer AR-4002, the analyzer used for determining sulfur in the streams with the highest sulfur levels (the carbonate tower feed and effluent streams) was never operated. Parts from the unit were used to keep the other analyzers operating.

Analyzer AR-4003, which was used to monitor the sulfur level in the ZnO tower bed and effluent, was apparently never reliable or sufficiently sensitive to the low levels of sulfur. Normally, when laboratory analyses indicated the presence of sulfur in the ZnO effluent, AR-4003 indicated much lower sulfur values or no sulfur at all. Since some sulfur poisoning of the methanation catalyst was definitely established after Run 47B, the laboratory chromatograph sulfur analyses are believed to be much more reliable than the results from the on-line chromatograph.

A discussion which covers the on-line chromatograph operation and some of the problems associated with this operation is presented in the Appendices, Book 4, Subsection 13.3.7.

SECTION 9

ENVIRONMENTAL CHARACTERIZATION OF PROCESS

An extensive environmental characterization program was conducted at the CO₂ acceptor gasification process pilot plant. Radian Corporation, under contract to CCDC, conducted the program with the major goal of establishing a data base which would be useful in projecting the nature and level of effluents from commercial CO₂ acceptor process plants. To accomplish this, the quantities and types of various organic compounds which are released during the gasification process and the fate of both major and trace elements, which enter the system primarily with the feedstock and the acceptor, were determined.

The studies definitely established the environmental cleanliness of the CO₂ acceptor process with regard to the production of oils, tars, phenols, and polynuclear aromatic compounds. In general, the measured concentrations of constituents detected were close to the lower accurate limit of the analytical procedures employed.

The total organic carbon content of the gasifier quench water averaged 2.8 mg/l. This can be interpreted as representing a hydrocarbon production rate of only 0.04 lb/ton MAF coal. Total phenols in the gasifier quench water occurred at an average production rate of 0.003 lb/ton MAF coal. The only organic species, in addition to phenols, detected in the gasifier quench water were benzene, naphthalene, indene, and toluene at levels of 900 µg/l, 270 µg/l, 16 µg/l, and 0.25 µg/l, respectively.

The combined ethane-ethylene concentration of the quenched gasifier product gas was 390 PPM. The only other hydrocarbons (except methane) that were in concentrations greater than 1 mg/m³ were benzene at 150 PPMV and naphthalene at 2-5 PPMV. At these low concentrations, all nonmethane hydrocarbons are expected to be hydrogenated or reformed in the methanation reactors.

Finally, naphthalene at a level of 1.2 wt. percent was the only extractable aromatic hydrocarbon adsorbed on the gasifier quench water solids at levels greater than 0.01 mg/g. This corresponds to less than 0.7 lb naphthalene/ton MAF coal. However, analysis of gases entering the quench tower revealed a naphthalene concentration corresponding to less than 0.05 lb/MAF ton.

When the aforementioned results are considered, it is not surprising that no oil sheens or scums were ever observed in the pilot plant quench water disposal pond and that no visual evidence was obtained of oil and tar formation in any equipment.

A special study was also conducted to establish the levels of toxic iron and nickel carbonyls in process and final product (SNG) streams. This was done because significant quantities of these volatile compounds could pose serious health hazards for both plant personnel and SNG consumers. The gas samples analyzed were taken at six points which were downstream of the gasifier quench system and which included the outlets of both methanation reactors. No attempt was made to analyze the gasifier product ahead of the quench system, since conditions in this stream are extremely unfavorable, thermodynamically, for carbonyl formation.

At all sampling points, the nickel carbonyl concentrations were found to be near or below the detection limits (1-3 PPB.) Iron carbonyl concentrations out of the quench tower were as high as 30 PPB. However, this is still well below the 8-hour occupational exposure threshold limit value of 50 PPB which has been established for nickel carbonyl. These results demonstrate that carbonyl production is not a problem for the CO₂ acceptor process.

The details and results of the Radian investigations, along with earlier trace element characterization studies conducted by the South Dakota School of Mines and Technology, are presented in Volumes 11 and 9, respectively, of this final report.^(1,2)

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- (1) Environmental Characterization - CO₂ Acceptor Process Gasification Pilot Plant, Period July, 1976-March, 1978, DOE Final Report No. FE/1734-44, Volume 11, Books 1, 2, and 3.
 - (2) Support Studies By South Dakota School of Mines and Technology - CO₂ Acceptor Process Gasification Pilot Plant, Period February, 1971-January, 1978, DOE final Report No. FE/1734-42, Volume 9, Books 1 and 2.

SECTION 10

TURBINE BLADE EROSION TESTS

10.1 TEST FACILITY

In 1971, Elliott Company designed and built a test fixture containing two rows of stationary blades to fit into a 6-inch diameter pipe. Solids-containing flue gas from the CO₂ Acceptor Process Pilot Plant at Rapid City, South Dakota, was passed through the fixture to determine the relative effect of the erosive particles on several different blade coatings.

So that the blading would only experience steady-state operation, flue gas was by-passed around the test section until the process was lined out; then a valve upstream of the test section was opened until the desired pressure ratio was established across the test fixture. Figure 10-1 presents a flow diagram of the test stand. Figure 10-2 shows the arrangement of buckets in the test fixture.

The blade coatings which were tested are proprietary materials, identified by Elliott Company as shown in Table 10-1.

<u>Coating</u>	<u>Vendor</u>	<u>Blade Nos.</u>	<u>Application</u>	<u>Description</u>
LC-1D	Union Carbide	3, 10	Detonating Gun	Chromium Carbide
L101	Union Carbide	2, 11	Detonating Gun	Cobalt, Nickel, Chromium, Tungsten
81-NS	Metco	5, 8	Plasma Spray	Chromium Carbide
LW-5	Union Carbide	4, 9	Detonating Gun	Tungsten Carbide
None	-----	1, 6, 7, 12	-----	-----

Table 10-1. DESCRIPTION OF BLADE COATINGS

10.2 TEST PROCEDURE

Each of the blades was weighed before and after each exposure, to determine the weight loss during the exposure to the particulate laden flue gas. In addition, the thickness of the thickest part of each blade and near the trailing edge was measured for each run to determine the change in profile dimensions.

Summarized test conditions are presented in Table 10-2. Isokinetic dust sampling was performed during Runs 30, 33B, and 39, and classification was made by Coulter Counter. For Runs 43A and 43B, dust was collected in Nomex bags and classified by Carrier Corporation using sieve sizing. The concentration for all runs was provided by Conoco except for Runs 44B and 45. No dust sampling was done for Runs 44B and 45, so a loading of 2 lbs. of dust per hour was assumed to have passed through the blades to provide a base for comparison.

Run No.	30	33B	39	42	43A	43B	44B	45
Barometer	13.05	12.99	13.08	---	13.04*	15.04*	15.04*	13.04*
Upstream Pressure	15.77	19.78	21.06	Varied	25.48	24.38	25.49	23.49
Upstream Temperature °F	560	600	680	530	543	550	540	560
Downstream Pressure	.0589	.1093	.0007	---	1.4427	1.2192	.0101	.0072
Pressure Ratio	1.203	1.51	1.61	Varied	1.76	1.71	1.80	1.80
Molecular Weight	31	52.95	32.5	---	32.5*	52.5*	52.5*	32.5*
Exposure	127	144	55.25	5.5	24.45	70.5	55.6	31.25
Gas Flow	8580	9594	12667	Varied	14192	15716	16990	14400
Gas Flow	701	833	1064	Varied	1192	1152	1427	1210
Particle Concentration								
Grains per standard ft ³	.055	.21	.04	---	1.03	1.32	.824	.972
Grains per actual ft ³	.034	.105	.027	---	.943	1.149	.698	.807
Pounds of dust per hour	.061	.245	.072	---	2.09	2.58	2.00*	2.00*
Total pounds of dust	8.35	35.28	3.98	---	51+	182+	107.2	62.5
Parts per million	87	294	68	---	1753	2240	1402	1653
Weighted Average Particle Size, microns	9	8	5	---	**	**	---	---
					532	474		

Table 10-2. OPERATING CONDITIONS

*Assumed, due to lack of data

**Based on Carrier sieve analysis

+Collected in Nomex bags downstream of test fixture

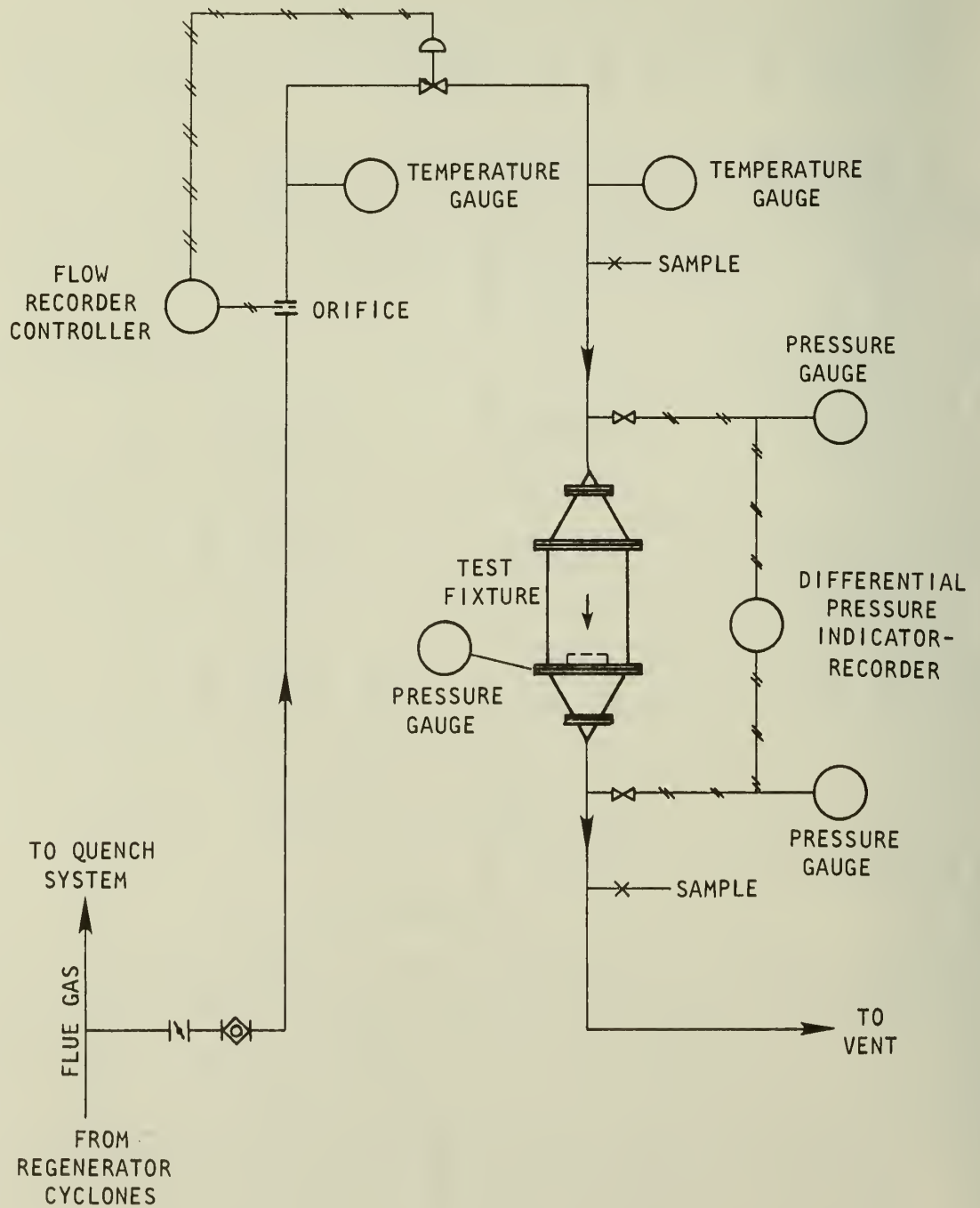


Figure 10-1. ELLIOTT TURBINE TEST FIXTURE FLOW DIAGRAM

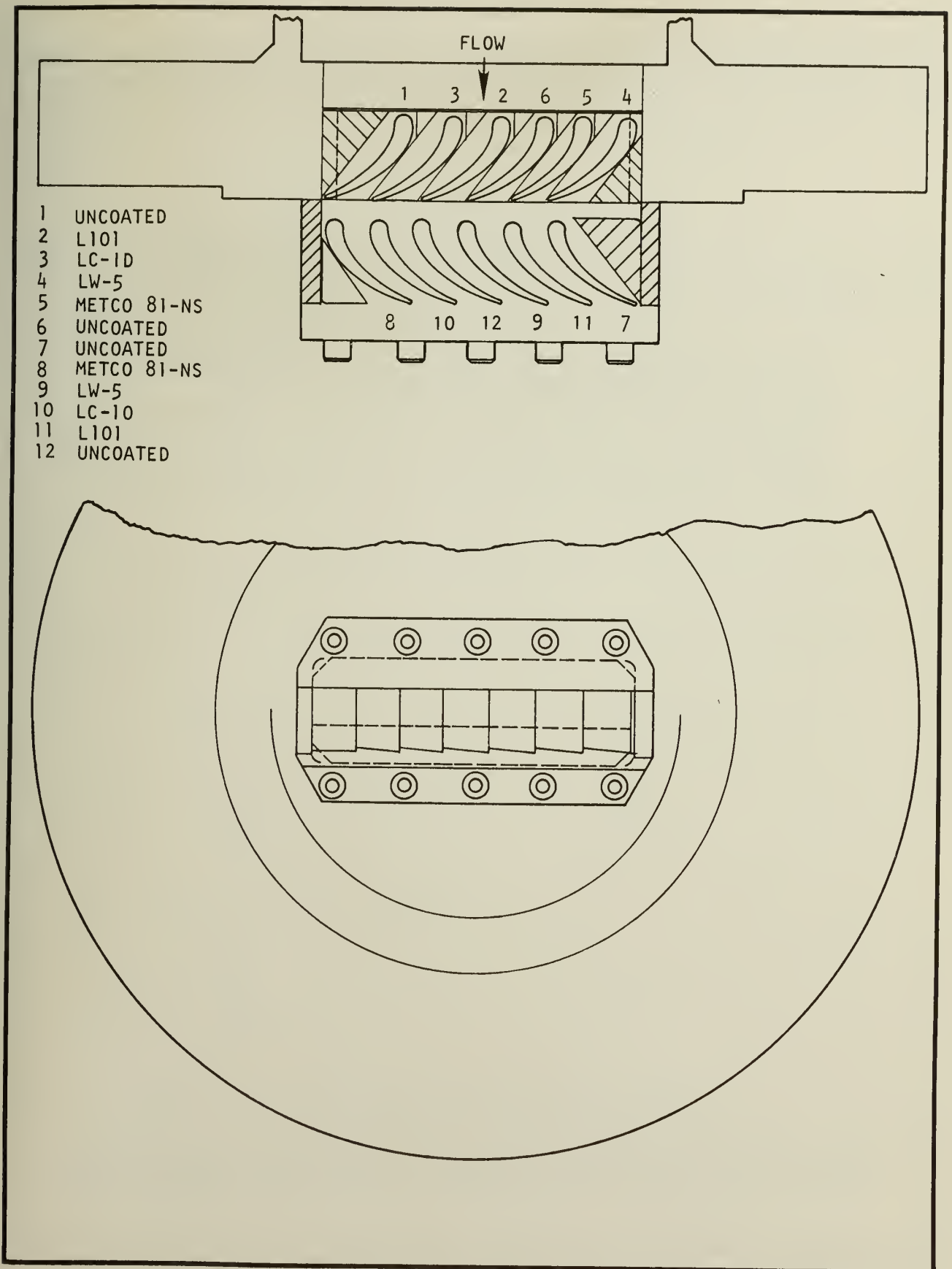


Figure 10-2. ARRANGEMENT OF BUCKETS IN ELLIOTT TURBINE TEST FIXTURE

10.3 TEST RESULTS

All of the buckets were returned to the Elliott Company for inspection and final conclusions. In their final report⁽¹⁾, Elliott Company rated the coatings as shown in Table 10-3. Figures 10-3 and 10-4 show typical test buckets with and without evident erosion.

10.4 CONCLUSIONS

While the test stand temperature at Rapid City (600°F) is considerably less than the anticipated 1200°F commercial turbine inlet temperature, Elliott Company has drawn the following conclusions:

- (1) That all four of the coatings used in this test provided a favorable erosion protection compared to the uncoated blade under the test conditions, based on weight loss data.
- (2) That Linde LC-1D coating on 19-1-DL base material offered more protection against erosion for the test conditions than any of the other coatings tested.
- (3) That the second row of blades experienced more erosion than the first row of blades.

(1) "Blade Coating Solid Particle Erosion Test (CO₂ Acceptor Process Plant)," Tech. Memo 336; C. H. Kusters, Elliott Co., Jeanette, PA, March 20, 1978.

NOTE

A one (1) indicates the best rating for erosion resistance, and a five (5) indicates the worse results in the erosive environment.

Rating based only on visual examination after total exposure:

- (1) Uncoated (except for Blade 12)
- (2) LC-1D
- (3) L101
- (4) 81-NS
- (5) LW-5

Rating based on visual examination, weight loss, and location in fixture:

	<u>First Row</u>	<u>Second Row</u>
(1)	LC-1D	LC-1D
(2)	L101	L101
(3)	81-NS	81-NS
(4)	LW-5	LW-5
(5)	Uncoated	Uncoated

NOTE

LW-5 coating would rank one or two notches higher if spalling had not occurred.

Rating based on the amount of coating or metal removed during the test period at Locations "A" and "B":

	<u>First Row</u>	<u>Second Row</u>
(1)	LC-1D	LW-5
(2)	LW-5	LC-1D
(3)	Uncoated	L101
(4)	L101	Uncoated
(5)	81-NS	81-NS

Final ranking based on all factors:

- (1) LC-1D
- (2) LW-5
- (3) L101
- (4) 81-NS
- (5) Uncoated

Table 10-3. EROSION RESISTANCE RELATIVE RANKING



Figure 10-3. ELLIOTT TURBINE TEST BUCKET NO. 12



Figure 10-4. ELLIOTT TEST TURBINE BUCKET NO. 9 SHOWING EROSION FROM RUN 33B

PLANT INNOVATIONS AND EQUIPMENT MODIFICATIONS

Due to the experimental nature of the CO₂ Acceptor Process Gasification Pilot Plant, modifications and innovative changes to the original design were often required to cope with unforeseen problems. The aspect of the process which posed the most difficult engineering problems was solids handling. The process requires the pneumatic transfer of large amounts of solids between reaction vessels, the maintenance of large fluidized beds in the vessels, and the processing of gases with many entrained solid particles. Related areas of the operation which demanded considerable effort were the preservation of delicate pressure balances throughout the high-temperature, high-pressure system, and the handling of highly corrosive gases.

The solutions to these problems involved many equipment modifications and, inseparably, the development of novel instrumentation setups to closely monitor and control the status of the system. The more important equipment modifications are outlined in this section. Instrumentation is covered in Subsection 11.3.

11.1 GAS DISTRIBUTORS

In the original design of the gasifier and regenerator, gas inlet lines and pneumatic transfer lines entered the vessels directly with no subsequent distribution inside the vessels. Prior to Run 7, (February, 1973) gas distributors were installed in both reactors; their performance is discussed in this subsection.

11.1.1 GASIFIER

11.1.1.1 Transition Section Gas Distributor

Prior to Run 7 an experiment was conducted in a glass model simulating the gasifier transition section. A 4-inch-ID glass section was added as a boot in combination with the 12-inch-ID upper section of the model. Size 6 x 16 mesh acceptor was added to the boot until approximately half of the boot was full. Then a char bed of 14 x 100 mesh char was built over the fluidized acceptor until an approximate 5-foot depth was obtained in the 12-inch section. Fluidization gas was added through both the boot and side distributors. Additional 6 x 16 mesh acceptor was then showered through the bed. By manipulating flows, a circulation rate of about 50 lbs per hour per square foot of bed was obtained.

The success of this experiment led to the installation of a ring-type distributor in the gasifier, to allow fluidization gas to be admitted to the gasifier transition section. An existing inlet line used to supply gas to the distributor had originally been designed to pneumatically transfer char from the devolatilizer to the gasifier. Since the devolatilizer never was used, the line was available for gas addition to the gasifier transition section. The side flow distributor ring design is shown in Figure 11-1. The distributor consists of a 4-inch, Schedule 40, Type 316 SS pipe bent to a 2-foot ID on the center line and blanked off halfway round to equalize the pressure distribution. To

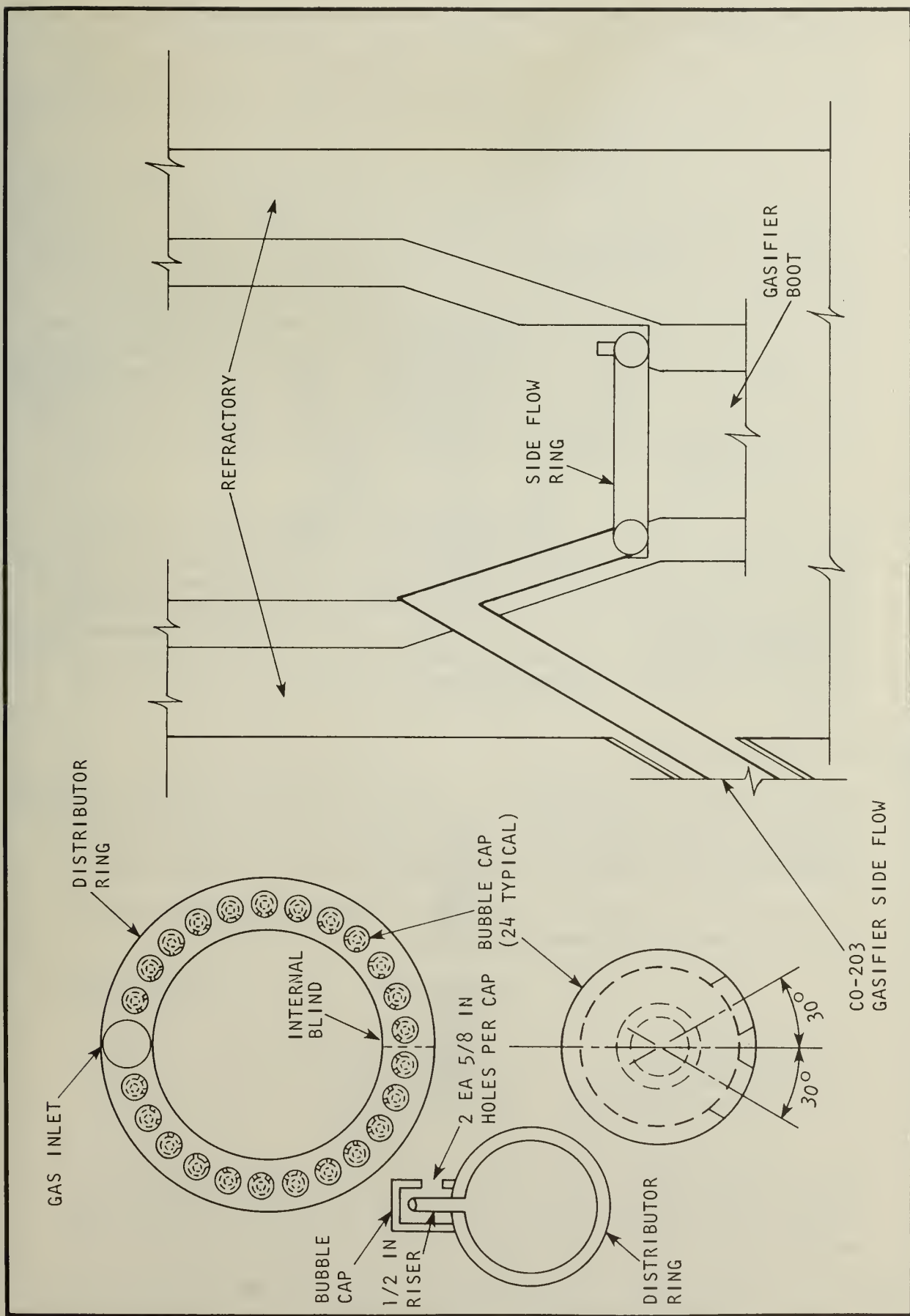


Figure 11-1. GASIFIER SIDE FLOW DISTRIBUTOR RING

prevent plugging during a shutdown, bubble cap-type nozzles on the distributor were constructed. The bubble caps consist of a 1/2-inch internal riser, open at the upper end and protected by a 1-1/2-inch capped pipe with two 5/8-inch holes drilled at its base. The 1-1/2-inch-diameter capped pipe with the two holes at its base is welded in place over the 1/2-inch vertical riser.

The basis of a design for the caps was a velocity of 100 feet per second in the vertical riser. In the gasifier, the flow rate was arbitrarily picked at approximately 40,000 SCFH, at 150 psig, at 1500°F. The inside diameter of a 1/2-inch Schedule 40 pipe produced a velocity of approximately 100 feet per second. The two 5/8-inch holes in the outer cap gave a velocity of 40 to 50 feet per second entering the char bed. The two 5/8-inch holes were drilled 60 degrees apart such that the gas flow would be toward the center of the vessel. These holes were placed low enough that the gas must turn 180 degrees before flowing perpendicularly into the vessel. This means that, upon shutdown, solids can go into the lower area of the bubble cap, but should not backflow into the 1/2-inch riser to the ring. There are 24 of these bubble caps equally spaced on the top of the 4-inch pipe distributor ring.

The initial operation with this distributor was entirely successful. There was one mishap that allowed char to flow back into the ring and back through the gas supply line. In this case, a differential pressure existed between the vessel and the piping. After shutdown, the distributor ring was disconnected and blown. The line was then reconnected and the ring was satisfactorily cleaned. After cleaning, there was little backflow or pluggage of this ring during any run. The gasifier sideflow ring, as originally designed, remained in service to the end of the project.

11.1.1.2 Boot Gas Distributor

Several boot gas distributors were used in an effort to eliminate deposits of dead-burned dolomite which formed during startup, as described in Volume 12, Book 2 Subsections 5.3.10.2 and 5.7.2.4 of this report. In general, each new design was based on experiments in a glass model.

The types of distributors, chronology of their use, and descriptive figure references are summarized below.

<u>Type</u>	<u>Used in Runs</u>	<u>Figure Number</u>
1. Capped pipe	7 through 20	11-2
2. Refractory Ball	21 through 22A	11-3
3. Plenum-Bubble Cap	22B through 40B	11-4
4. Small Ring-Bubble Cap	41A through 46A	11-5
5. Large Ring-Bubble Cap	46B through 47B	11-6

The start-up deposits never were eliminated entirely. Certainly, improved distributors can be built in the much larger boot of a commercial gasifier which will permit more geometric flexibility than was possible in the 18-inch diameter boot of the pilot plant.

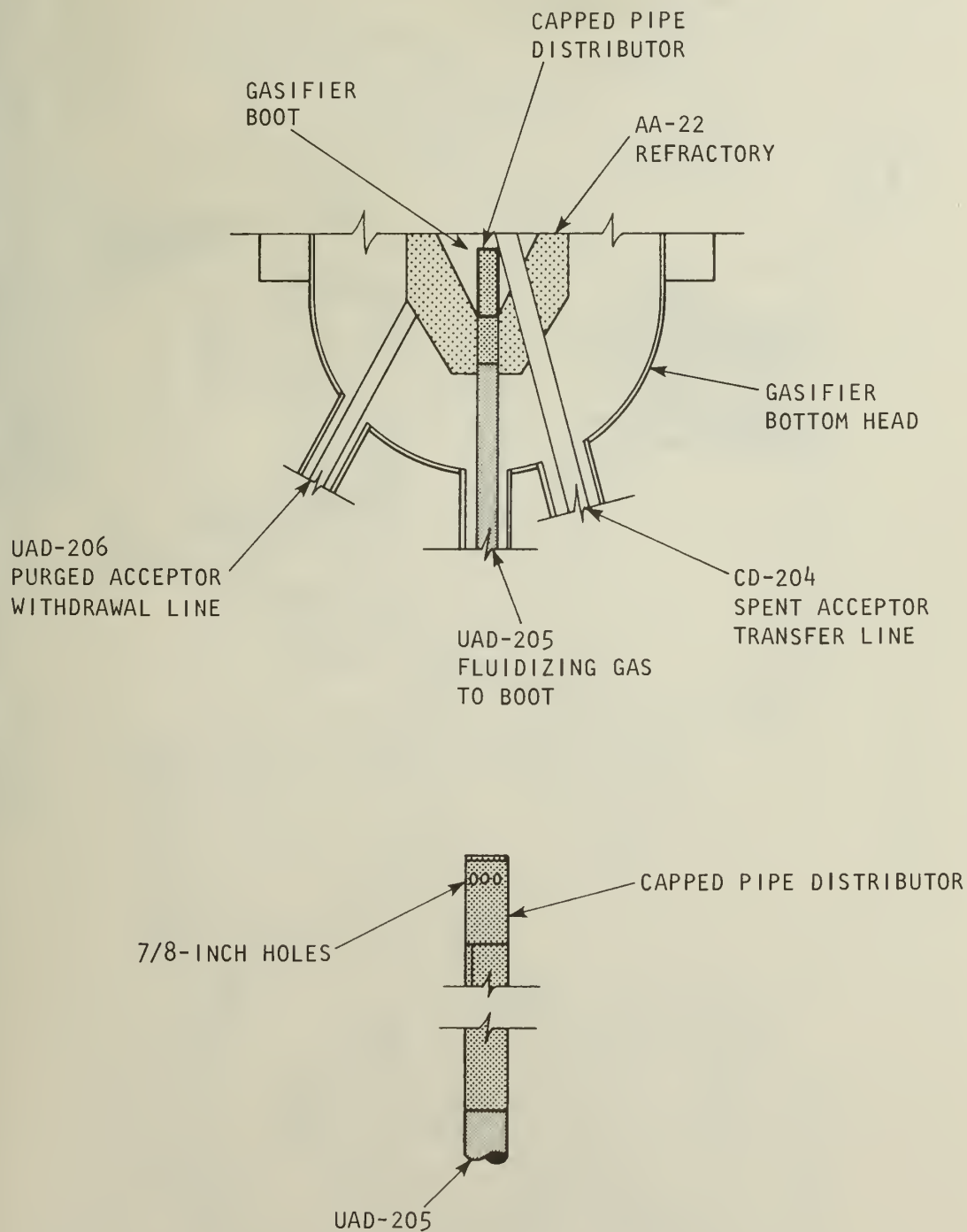


Figure 11-2. GASIFIER CAPPED PIPE BOOT DISTRIBUTOR

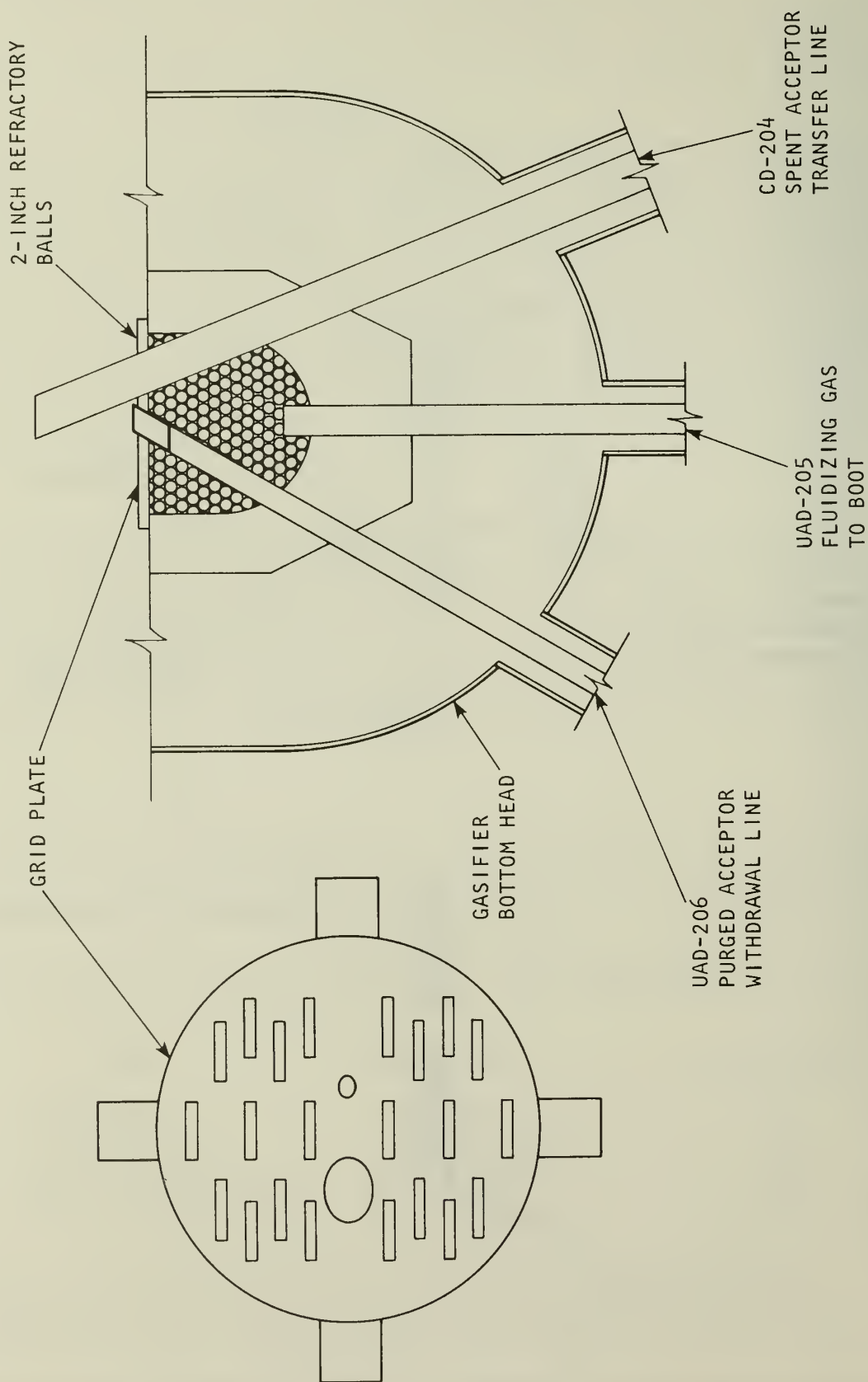


Figure 11-3. GASIFIER GRID AND BALL BOOT DISTRIBUTOR

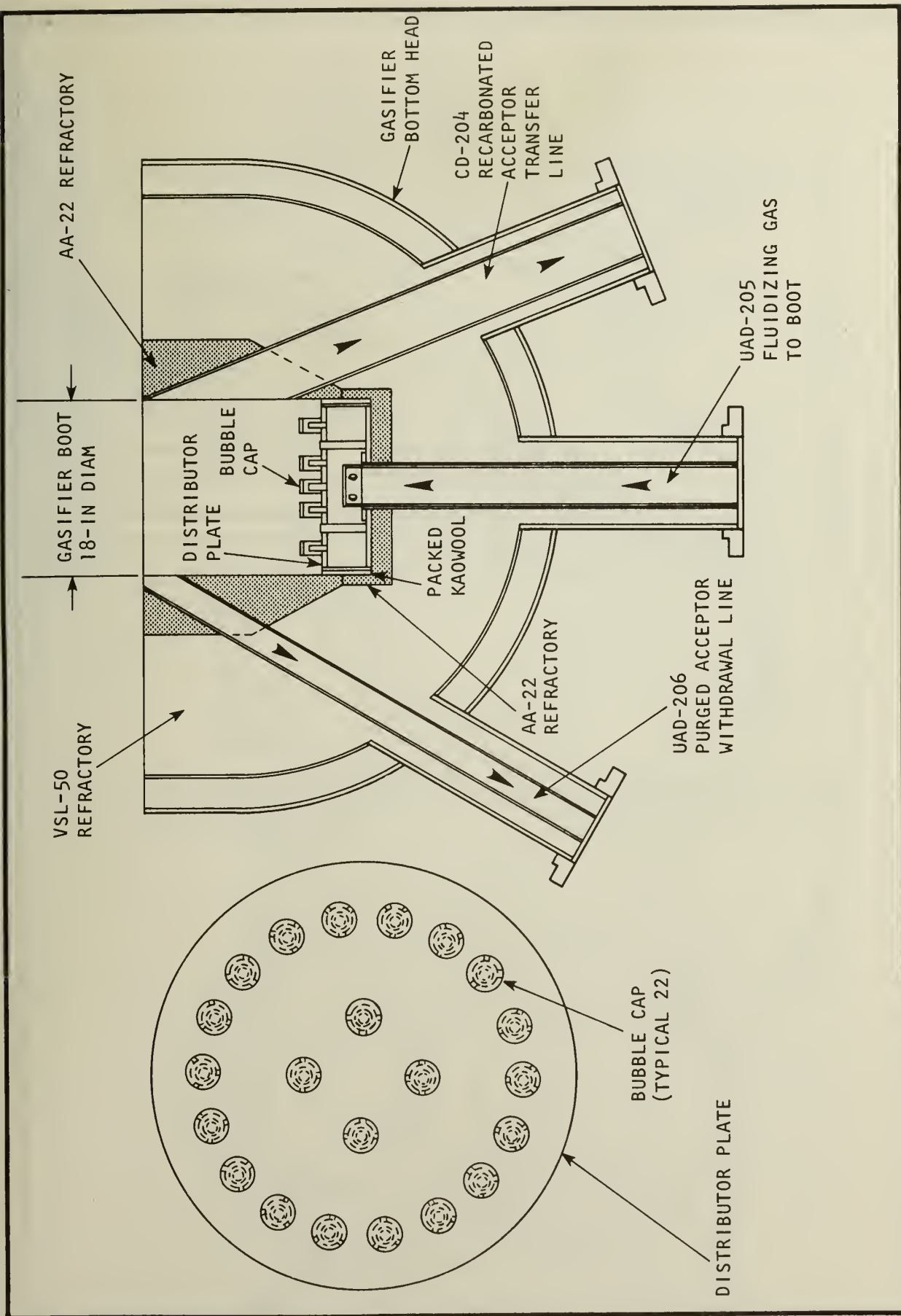


Figure 11-4. GASIFIER PLENUM CHAMBER WITH BUBBLE-CAPS BOOT DISTRIBUTOR

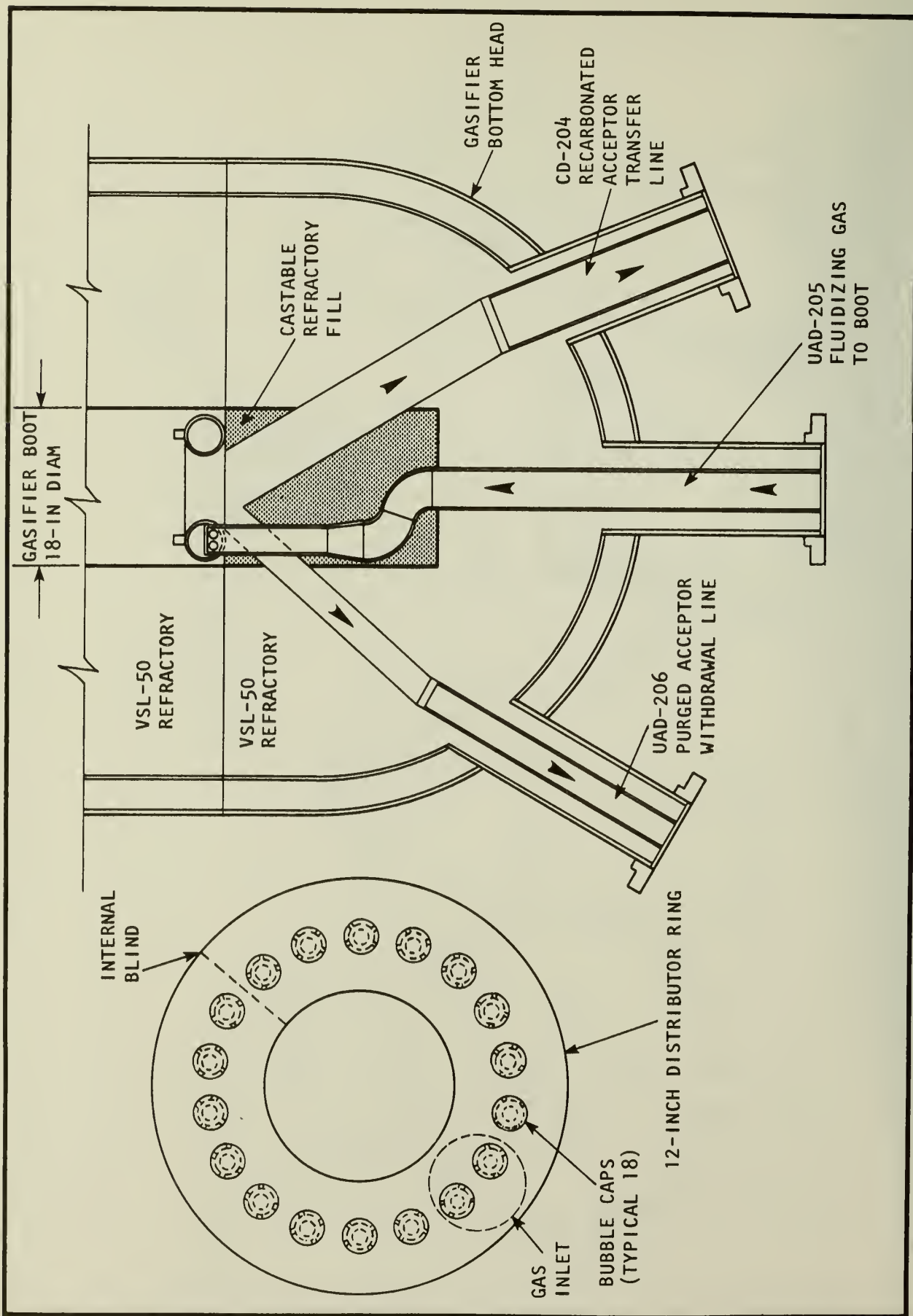


Figure 11-5. GASIFIER 12-INCH RING-TYPE BOOT DISTRIBUTOR

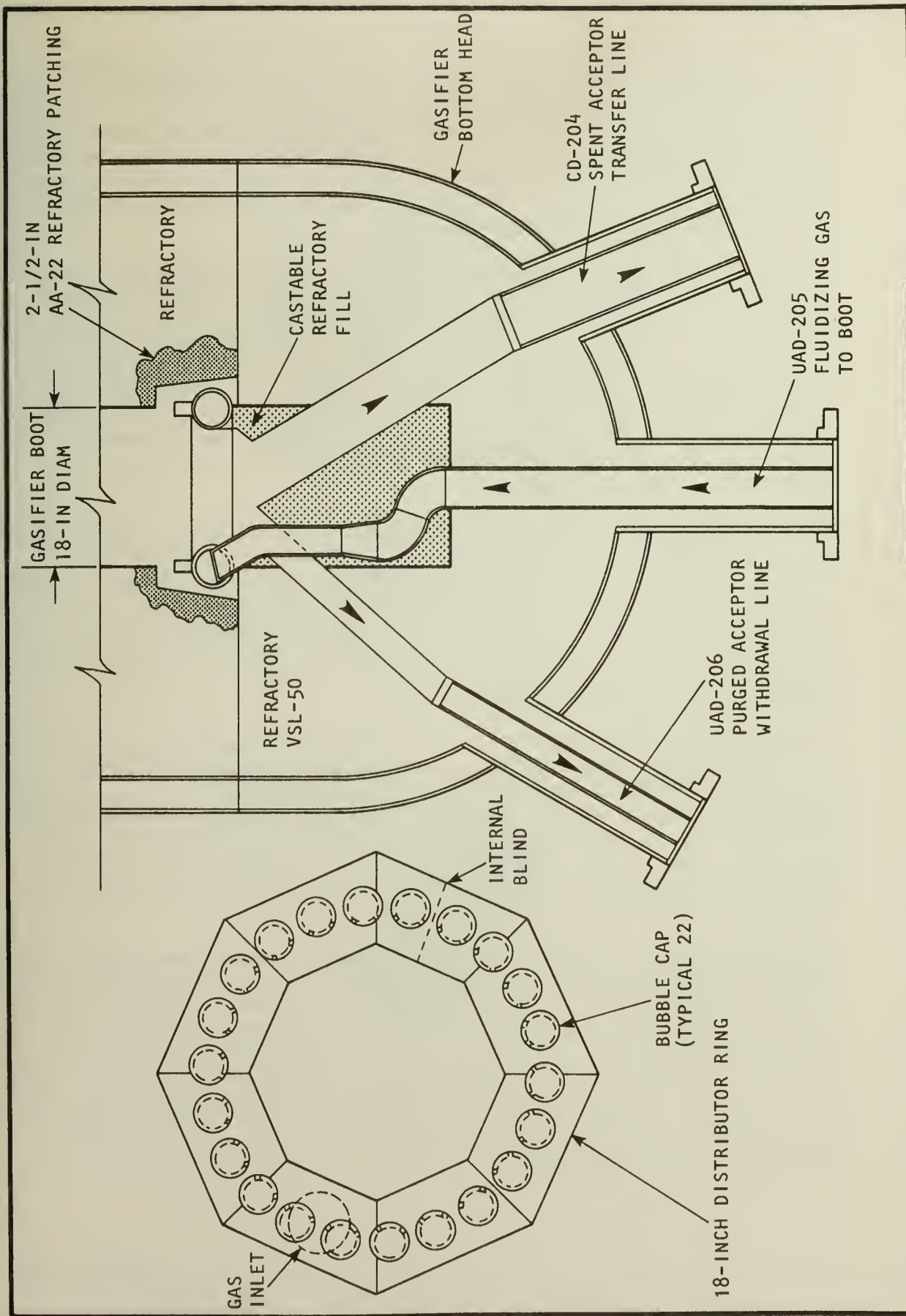


Figure 11-6. GASIFIER 18-INCH RING-TYPE BOOT DISTRIBUTOR

The design of the first distributor to be installed in the regenerator was a capped pipe welded onto the air inlet into the regenerator. This line entered the vessel at a 60-degree angle from the horizontal. Nine 5/8-inch holes were drilled perpendicular to the pipe and spaced such that there were fewer holes facing upwards towards the refractory wall. (See Figure 11-7.) The placement of holes was made to avoid excessive erosion of the refractory. The capped pipe distributor was installed prior to Run 7 in February, 1973.

In initial use, the capped pipe distributor in the regenerator caused a high rate of acceptor attrition, primarily because of an excessive velocity of flow through the air line. Velocities through the nine 5/8-inch holes exceeded 400 feet per second. During the shutdown following Run 7, the openings in the regenerator distributor were increased from 5/8 to 3/4 inch. For subsequent runs, the velocity in the regenerator was limited to 150 feet per second through the openings. Under these conditions, attrition was minimized but not eliminated. Therefore, the decision was made in mid-April, 1973, to install a different type of distributor.

Based on the success with the sideflow gas distributor ring in the gasifier, the decision was made to install a similar system on the air inlet line in the bottom of the regenerator. This distributor is identical in all respects to the gasifier sideflow ring distributor in Figure 11-2, with the exception that the 4-inch ring and the risers are made of Type 310 stainless steel. The installation of this distributor in the regenerator is shown in Figure 11-8. The ring-type distributor was installed prior to Run 9 in April, 1973.

The same design was used for the regenerator distributor ring as for the gasifier sideflow ring, because a nominal air flow into the regenerator was 40,000 SCFH at a slightly higher temperature than in the gasifier. However, during later runs, when more heat was necessary in the regenerator, air flow to the distributor was increased to 60,000 cubic feet per hour. Even at these rates, the velocity entering the regenerator through the two 5/8-inch holes in each bubble cap did not exceed 70 to 75 feet per second.

Although the ring distributor in the regenerator was never changed, except to be replaced by an identical ring, the diameter of the regenerator was reduced from 33 inches to 24 inches prior to Run 42. Since the interior of the regenerator ring was also 24 inches, the vessel diameter reduction effectively put the gas distributor around the edge of the fluidized bed instead of inside the bed. This change eliminated "dead spots" of unfluidized acceptor in the bottom of the reactor and thereby also eliminated the customary acceptor deposits which previously had formed around the outside of the distributor ring. No further gas distribution changes were made in the regenerator.

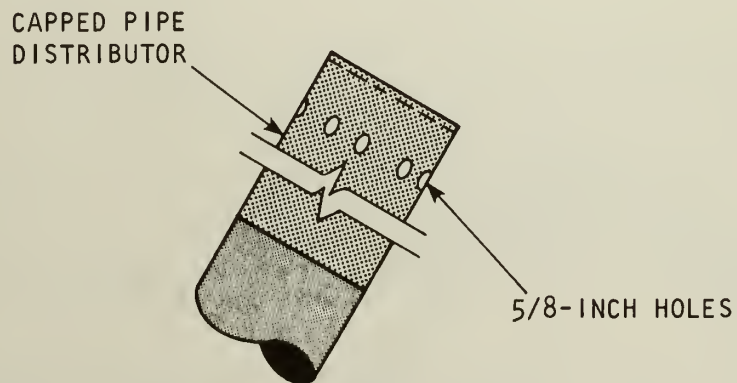
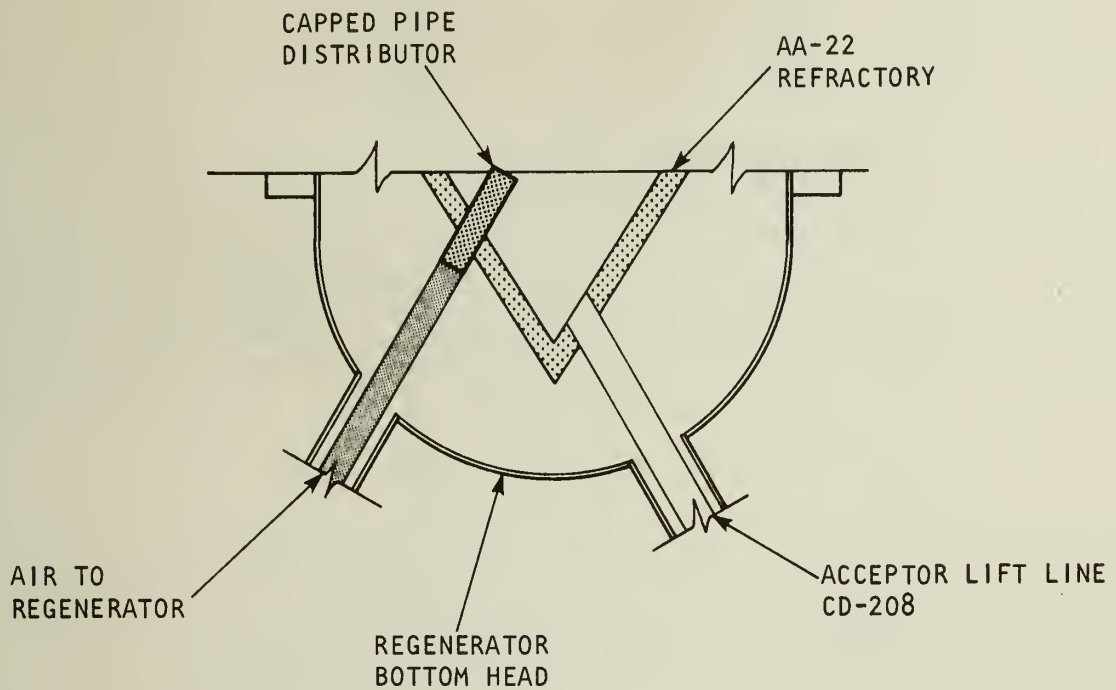


Figure 11-7. REGENERATOR CAPPED PIPE AIR DISTRIBUTOR

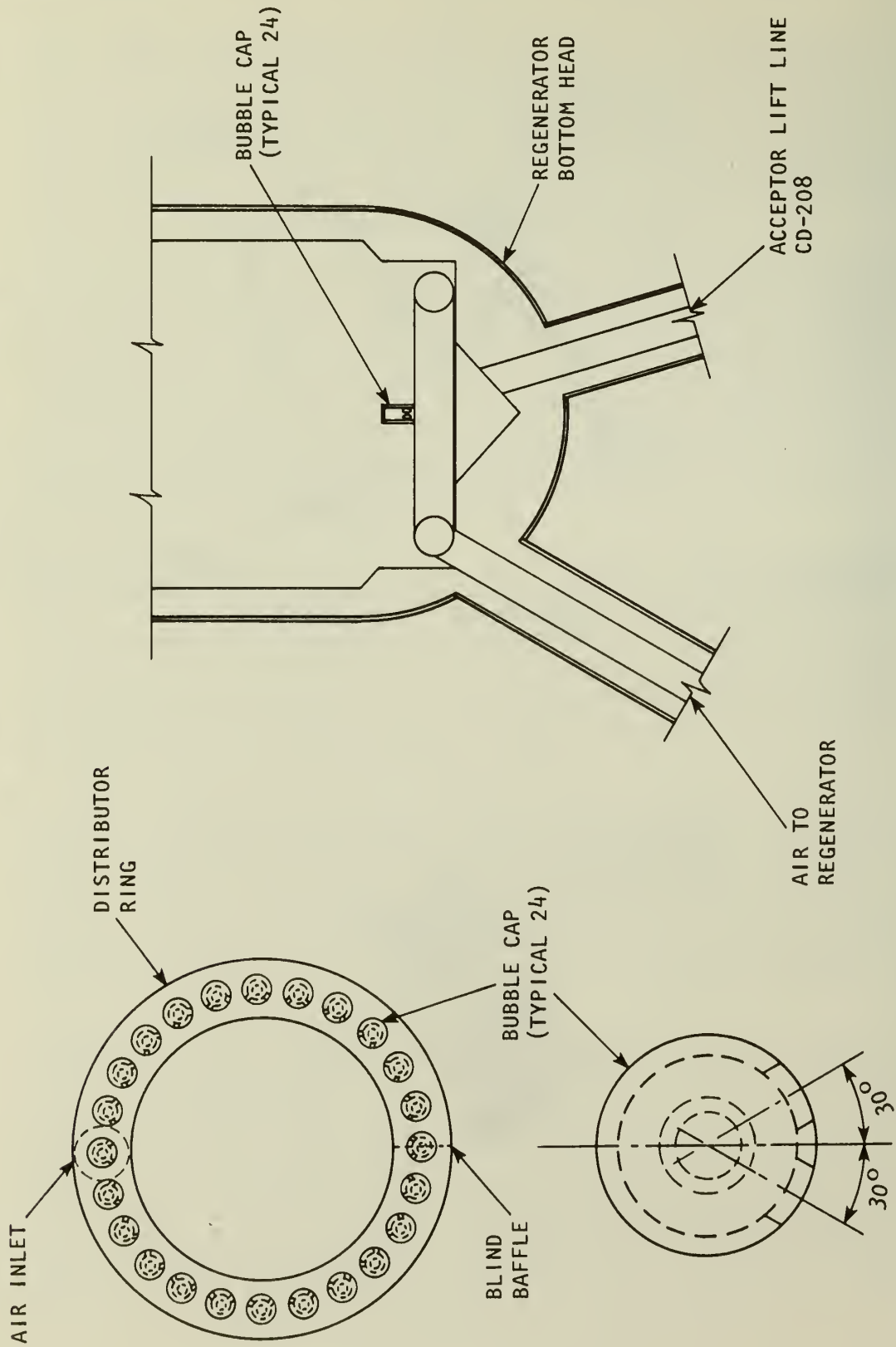


Figure 11-8. REGENERATOR AIR DISTRIBUTOR RING

Prior to Run 38C in August, 1976, it was not uncommon to experience problems maintaining a char standleg seal above the spent char transfer valve, LCV-2002, in the CO-202 transfer line. Since LCV-2002 is a butterfly valve, char lift gas from the char wye had a tendency to leak back past LCV-2002 during system pressure fluctuations. This occurred even with the valve fully closed and had the effect of blowing the char in the standleg back into the gasifier. Once the solids seal above LCV-2002 had been lost, lift gas would continue to flow up CO-202 to the gasifier, preventing the line from refilling and the seal from reforming. So, during Run 38B shutdown, another butterfly valve, or "wafer valve," which was manually operated and had closer tolerances than LCV-2002, was installed directly below LCV-2002. This arrangement allowed both valves to be closed at once to greatly improve the gas seal in the char standleg. After installation, the "wafer valve" performed as expected and caused no unexpected problems. The "wafer valve" assembly is shown in Figure 11-9.

11.3 QUENCH TOWER SYSTEMS

All hot gas quench systems at the CO₂ Acceptor Process Gasification Pilot Plant had the same basic configuration when construction of the facility was complete. The quench towers were basic vertical plate-and-donut-type vessels. Each tower was equipped with a quench water separator to remove tars and oils from the quench water before it was recirculated through the tower. Alterations to the regenerator and gasifier quench systems are discussed in this section. The devolatilizer quench system was never put into service and is not discussed. Quench tower inlet modifications can be found in Section 11.4 which deals with quench tower inlet venturis.

11.3.1 REGENERATOR QUENCH SYSTEM

The design of the Regenerator Quench System as originally installed was similar to hot gas quench systems found in oil refineries. The system contained a vertical plate-donut-type quench tower equipped with a quench water separator. The ash and attrited acceptor fines which escaped the cyclones upstream of the quench tower tended to settle out in the quench tower separator. As a result, the quench water separators became laden with solids and would become inoperative after short periods of operation. A flow sheet of the quench tower equipped with a quench water separator is shown in Figure 11-10.

The problem with fines collecting in the flue gas quench water separator was effectively solved prior to Run 7. Since no tars or oils were ever found in the regenerator flue gas, no flue gas quench water separator was needed. As a result, the flue gas quench water separator was removed from the system.

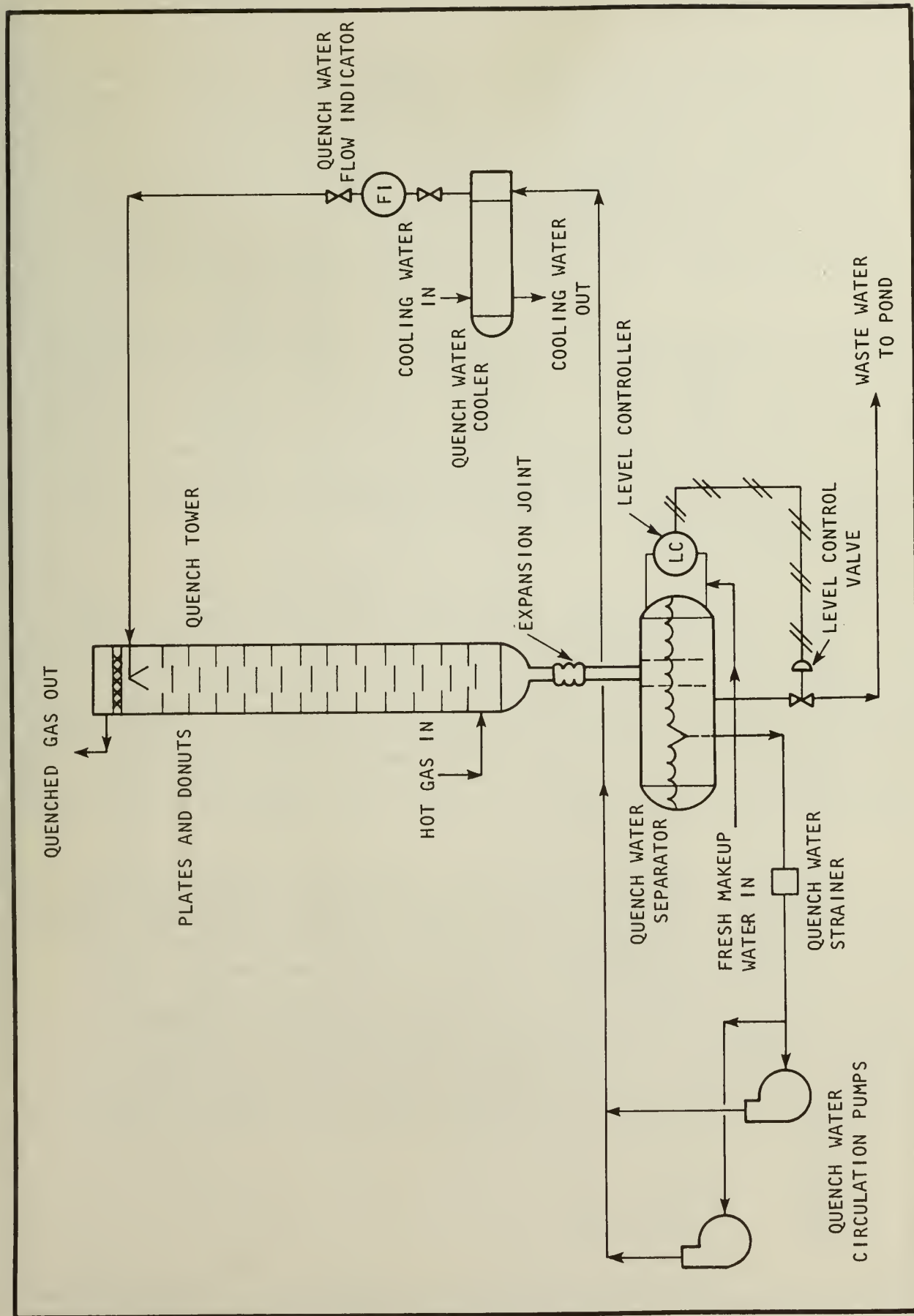


Figure 11-10. QUENCH TOWER EQUIPPED WITH QUENCH WATER SEPARATOR

However, solids fines that entered the quench tower still had to be removed. This was accomplished by removing one-half of the plates and donuts in the tower, replacing the dish-shaped bottom of the tower with a cone-shaped bottom, moving the hot gas inlet to slightly below the base of the remaining plates, and equipping the tower with a level controller. The bottom half of the tower effectively became the quench water separator. As the quench water laden with solids collected in the lower half of the tower, the solids settled to the bottom and were drawn off through the quench water level control valve. The amount of slurry flushed from the bottom of the tower was equal to the amount of makeup water admitted to the system. Quench water to be recirculated was drawn off near the top of the column of water held in the lower half of the tower.

Although use of the bottom of the tower as a separator did greatly improve the performance of the quench system, it did not eliminate periodic buildup of fines in and around the waste water outlet in the cone-shaped bottom of the tower. The fines buildup invariably caused plugs in the quench water outlet line. As a result, a bypass was installed around the water outlet level control valve and assorted high-pressure water blast lines and purges were installed. Coupled with a second external gas cyclone to remove solids fines before they reached the quench tower, the modified quench system performed satisfactorily while the plant was in a steady-state condition.

Upsets in the plant that affected process flows to the regenerator sporadically caused solids plugs in the bottom of the quench tower. During an upset in the system, erratic process flows would "burp" large amounts of acceptor from the regenerator fluidized bed into the overhead gas line. Some of the acceptor would be dropped out by the in-line gas cyclones, L-202 and L-202A; however, it was not unusual to get several hundred pounds of acceptor in the bottom cone of the quench tower. Unless action to cut makeup in the quench system or to flush the tower cone bottom was taken immediately, the quench tower would fill with water. Quench water would then find its way to the recycle gas compressors and eventually into most of the gas recycle lines.

To eliminate the problem of quench tower overflows, an emergency drain was installed in the side of the quench tower slightly below the normal water level in the tower. The level control valve in the emergency drain was connected to the same level controller as the primary level control valve in the bottom outlet of the tower; however, the emergency drain valve would not operate until the primary valve was effectively full open and the level in the tower was continuing to rise. The emergency drain arrangement eliminated quench tower overflows and allowed the primary level control valve and piping in the bottom of the tower to be taken out of service for repair whenever necessary. The final basic configuration of the regenerator quench system can be found in Figure 11-11.

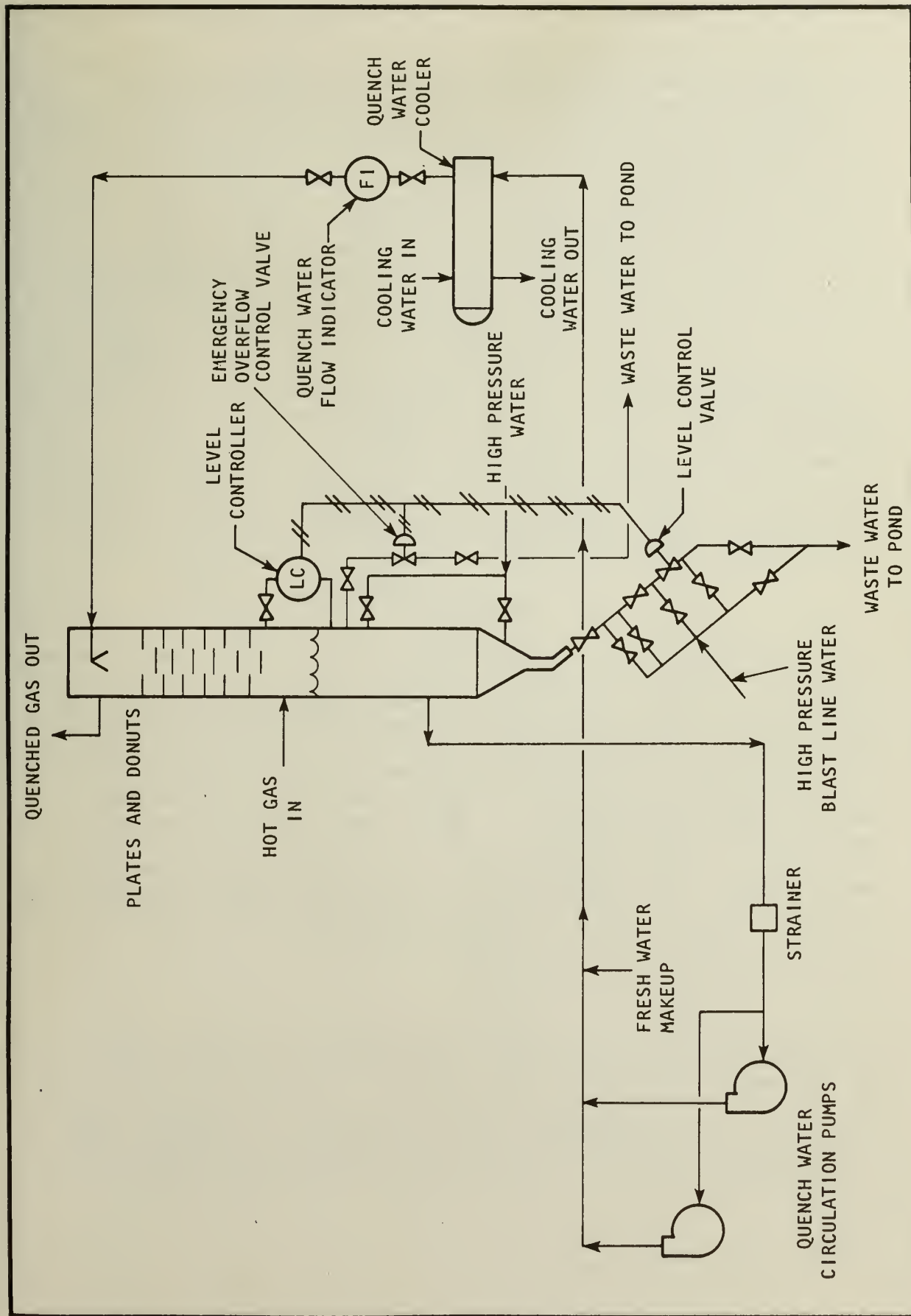


Figure 11-11. QUENCH TOWER FINAL CONFIGURATION

11.3.2 GASIFIER QUENCH SYSTEM

The Gasifier Quench System was similar in most respects to the regenerator quench system, with the exceptions of a gasifier gas venturi scrubber at the gas outlet of the gasifier quench tower and a foul water stripper to handle the liquid effluent from the venturi scrubber. The gasifier gas venturi scrubber and the foul water stripping system were originally included in the gasifier quench system design, to strip the large amount of sulfur compounds expected in the gasifier quench water before the quench water was discharged from the plant. However, solids fines which caused so many problems in the quench systems made the foul water stripper system virtually inoperative. It eventually was removed from the system. A flow diagram with the foul water stripper and venturi scrubber is shown in Figure 11-12.

Since the gasifier quench tower, equipped with a gasifier quench water separator, was required to handle as many solids fines as the regenerator quench system, its service history was nearly identical to that of the regenerator quench tower. The quench water stripper was scrapped. Half of the plates and donuts were removed from the quench tower, the bottom of the quench tower was modified, and a level controller was added to the tower so the lower portion could be used as a separator. The final configuration of the gasifier quench system was identical to that of the regenerator and can be found in Figure 11-11.

11.4 VENTURIS

Since the first run, buildup of solids in the reactor overhead lines near the inlet of the quench towers was a continuing problem. Initially, buildups in the line between the ash/fines removal cyclone, L-202, and the regenerator quench tower caused serious pressure upsets in the system, which occasionally resulted in plant shutdown. Buildups at the inlet to the gasifier quench tower also occurred during early runs; however, solids buildups in the regenerator quench inlet usually overshadowed those in the gasifier system. Not until after revisions were made to the regenerator quench system, curtailing shutdown-causing upsets in that system, did solids restrictions at the gasifier quench tower inlet become serious. The in-line gas venturi was used to help eliminate solids restrictions in both the gasifier and regenerator quench inlets. The histories of the venturis in both systems follow.

11.4.1 REGENERATOR QUENCH TOWER VENTURIS

The first in-line gas venturi used at the Rapid City facility was 4 inches in diameter and was installed in a horizontal position in the inlet to the regenerator quench tower prior to Run 6. During the first five runs, several different methods of introducing gas to the quench tower had been tried. Each new setup resulted in a plug forming in a different shape at a different location. It was hoped that a horizontal in-line venturi with water injected into its throat would eliminate the problem.

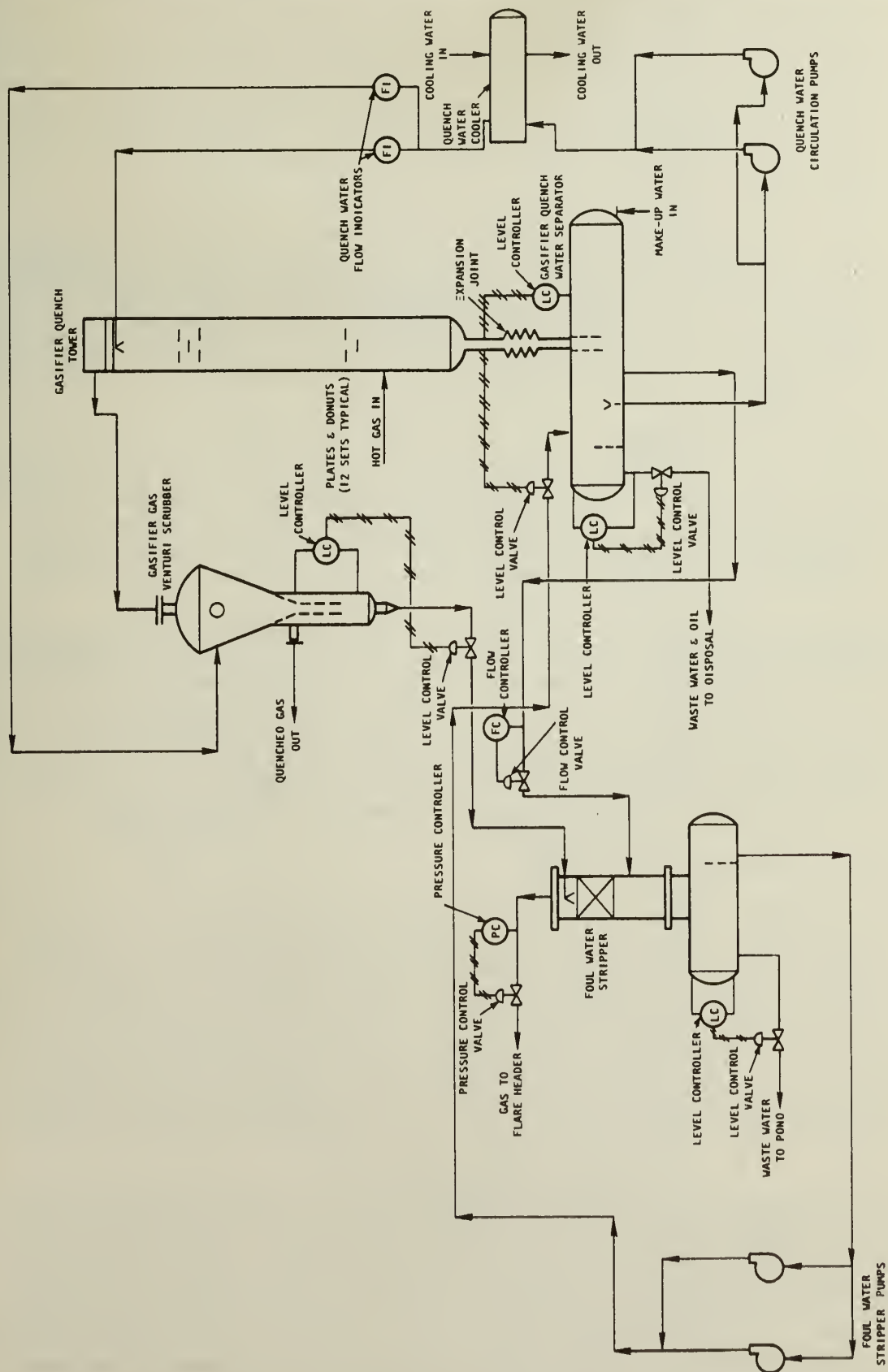


Figure 11-12. GASIFIER QUENCH SYSTEM EQUIPPED WITH FOUL WATER STRIPPER

The first run with the horizontal venturi was not encouraging. Solids that had previously collected at the quench tower inlet now collected in the venturi. During subsequent runs with the venturi in the horizontal position, the water injection point was moved from the venturi throat, first downstream and then upstream. In all cases, plugs continued to form. Prior to Run 12, the venturi was moved from a horizontal pipe run to a vertical pipe run in the same line. A manual rod-out device downstream of the venturi was also installed when the venturi was repositioned.

Repositioning of the regenerator venturi did not eliminate plugging, but it did reduce the amount of buildup upstream of and in the venturi. Although solids continued to collect downstream of the venturi, the newly installed rod-out successfully kept the inlet to the quench tower open. Although having to manually rod out the inlet of the tower was far from an ideal situation, no subsequent shutdowns resulted from a restriction at the regenerator quench tower inlet.

During Run 17B shutdown, a second larger gas venturi was installed in parallel with the existing regenerator venturi. The new 6-inch venturi replaced an experimental mechanical gas-water contacting device that proved inoperable. During the installation of the second venturi, sufficient valving was also installed to allow either venturi to be isolated and removed for cleaning during plant operation.

The two parallel venturis in the regenerator quench inlet line remained in service to the end of the project. Solids buildups below the venturi that had been removed by manual rodding were later successfully eliminated by the installation of a second in-line gas cyclone, which greatly reduced the solids loading in the gas to the venturis, and the addition of "Betz" chemical inhibitors to the water injected to the venturis. The "Betz" chemical addition is completely discussed in Section 7. A sketch of the regenerator quench inlet setup is shown in Figure 11-13.

11.4.2 GASIFIER QUENCH TOWER VENTURI

The gasifier quench tower inlet venturi was first installed during Run 23 shutdown. Success of the regenerator quench venturis in reducing quench tower inlet deposits (which were now plaguing the gasifier quench system) had been so encouraging that L-315B, one of the regenerator quench venturis, was relocated to the gasifier overhead line immediately upstream of E-301, the gasifier quench tower. L-315B was installed in a vertical position directly under the water-jacketed portion of the gasifier overhead line. Piping from the venturi to the quench tower was horizontal and equipped with manual rod-outs. Water was injected to the venturi throat.

Unfortunately, during Run 24, deposits that had been forming at the quench tower inlet now formed in the diverging section of the venturi and the downstream horizontal piping to the quench tower. Run 24 was terminated when chunks of deposits that were loosened from the venturi diverging section and the associated piping became lodged in the 4-inch-to-2-inch reducer at the quench tower inlet. The resulting plug stopped product gas from the gasifier from being vented and necessitated an emergency shutdown.

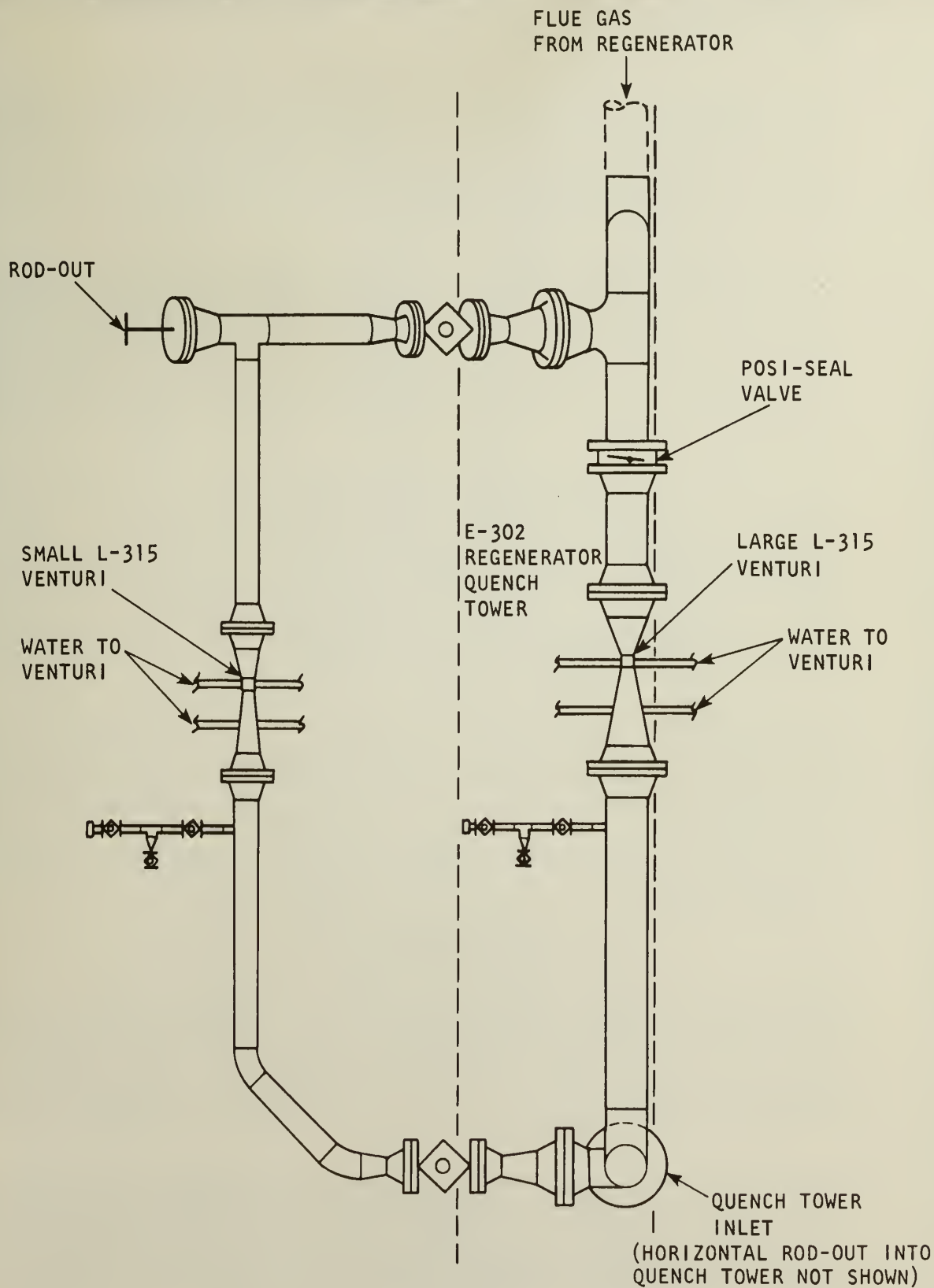


Figure 11-13. REGENERATOR QUENCH TOWER INLET SETUP

Between Runs 24 and 25 a larger 4-inch nozzle was installed on the gasifier quench tower, and the venturi was installed vertically, immediately upstream of the nozzle.

A horizontal rod-out for the new 4-inch nozzle was also installed. The old 2-inch nozzle was converted to a bypass for the venturi scrubber, to be used in the event the venturi became plugged while the horizontal rod-out into the quench tower was being used. During Run 26A, deposits continued to form below the venturi; however, the quench tower inlet was kept open by use of the rod-out device.

A series of tests was run before Run 26A to study the water distribution in the venturi. As a result of the tests, the quench venturi in use on the gasifier quench systems was modified to have six 3/16-inch-diameter water inlet nozzles in the venturi throat and diverging section, as opposed to the original two 3/8-inch opposing nozzles. Although the modification did not solve the solids deposit problems, a decrease in solids buildup was noted. A sketch of the basic venturi design can be found in Figure 11-14.

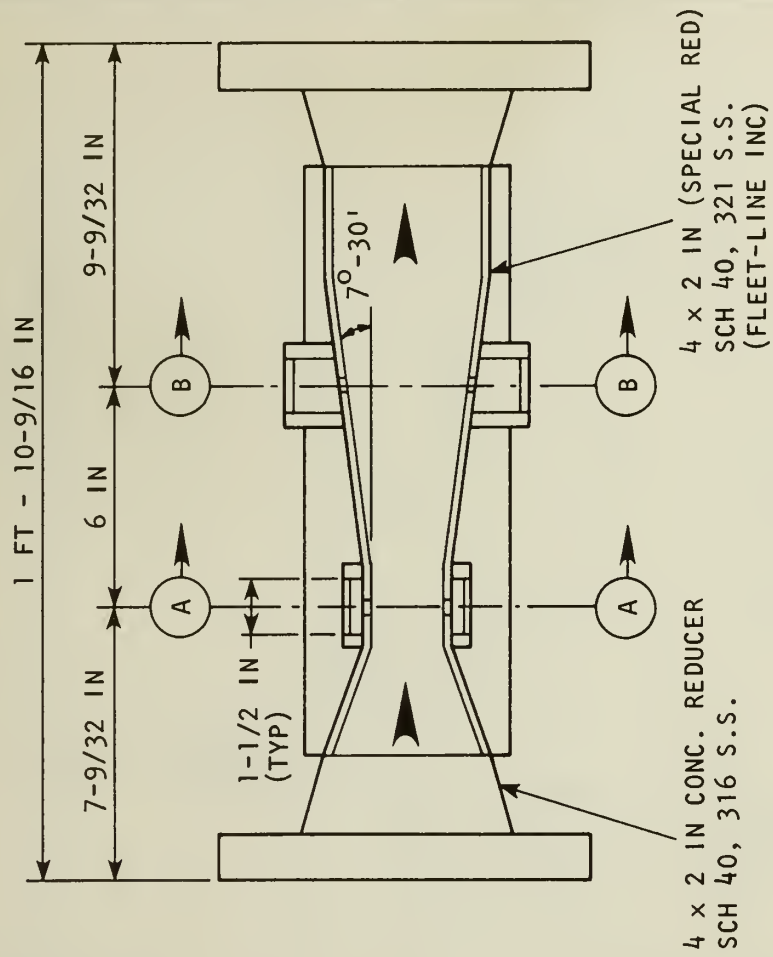
Before Run 26B, a second rod-out was installed below the gasifier quench venturi in a vertical position to rod up through the venturi. Also, since chemical analyses showed the deposits to be mostly calcium, the calcium-rich high-pressure potable water to the venturi was replaced with softened boiler feedwater treated with a calcium dispersant. However, plugs continued to form and manual rodding was necessary to prevent total plugging. The gasifier quench venturi was also renamed L-317 at this time. A sketch of the gasifier quench inlet venturi installation is shown as Figure 11-15.

During subsequent runs, no mechanical modifications were made to the gasifier venturi. Different chemical additives to the venturi water were tested until a suitable chemical, Betz DE-670, was found to successfully reduce buildup in the venturi and downstream piping. Also, the addition of the gasifier external cyclone in the gasifier product gas line upstream of the venturi substantially reduced the solids loading on the venturi. By Run 31, solids deposits at the gasifier quench tower no longer presented a serious problem.

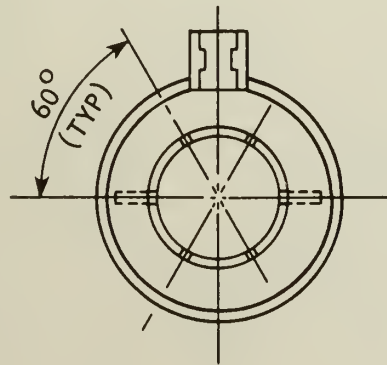
11.5 ROD-OUTS

Simple rod-out devices, such as those shown in Figure 11-16, are employed for cleaning out sample points during a run. The flange which attaches the rod-out to the sample point is interchangeable to fit different sample points. The Conax fitting eliminates system pressure from blowing back through the rod-out device. The ball valve makes it possible to remove or replace the rod safely and quickly.

Figure 11-16 also depicts a typical side-entry pressure probe with a thermocouple installed. During normal operation, restricted taps are first blown with high-pressure bottled nitrogen. If the restriction is not cleared by blowing, the thermocouple can be used as a rod-out. The ball valves and Conax fitting allow the thermocouple to be safely replaced during a run. A rod with a drill-bit tip can also replace the thermocouple whenever necessary to clear severe plugs.

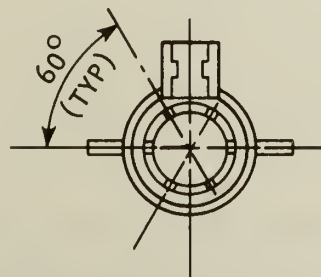


(6) 3/16-IN-DIAM
DRILLED HOLES



SECTION B-B

(6) 3/16-IN-DIAM
DRILLED HOLES



SECTION A-A

Figure 11-14. L-317 GASIFIER QUENCH INLET VENTURI

PRODUCT GAS
FROM GASIFIER
EXTERNAL CYCLONE

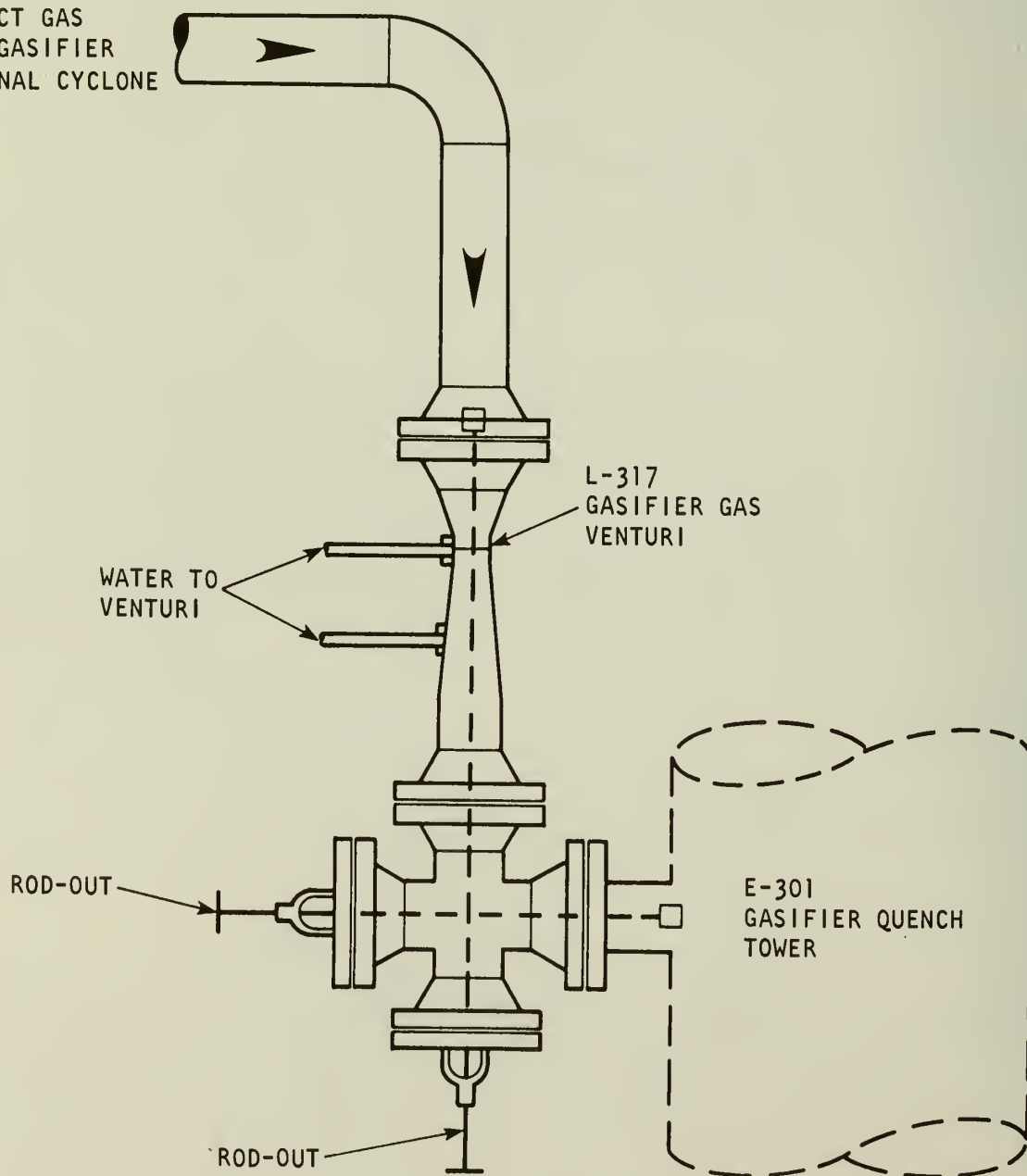


Figure 11-15. GASIFIER QUENCH TOWER INLET SETUP

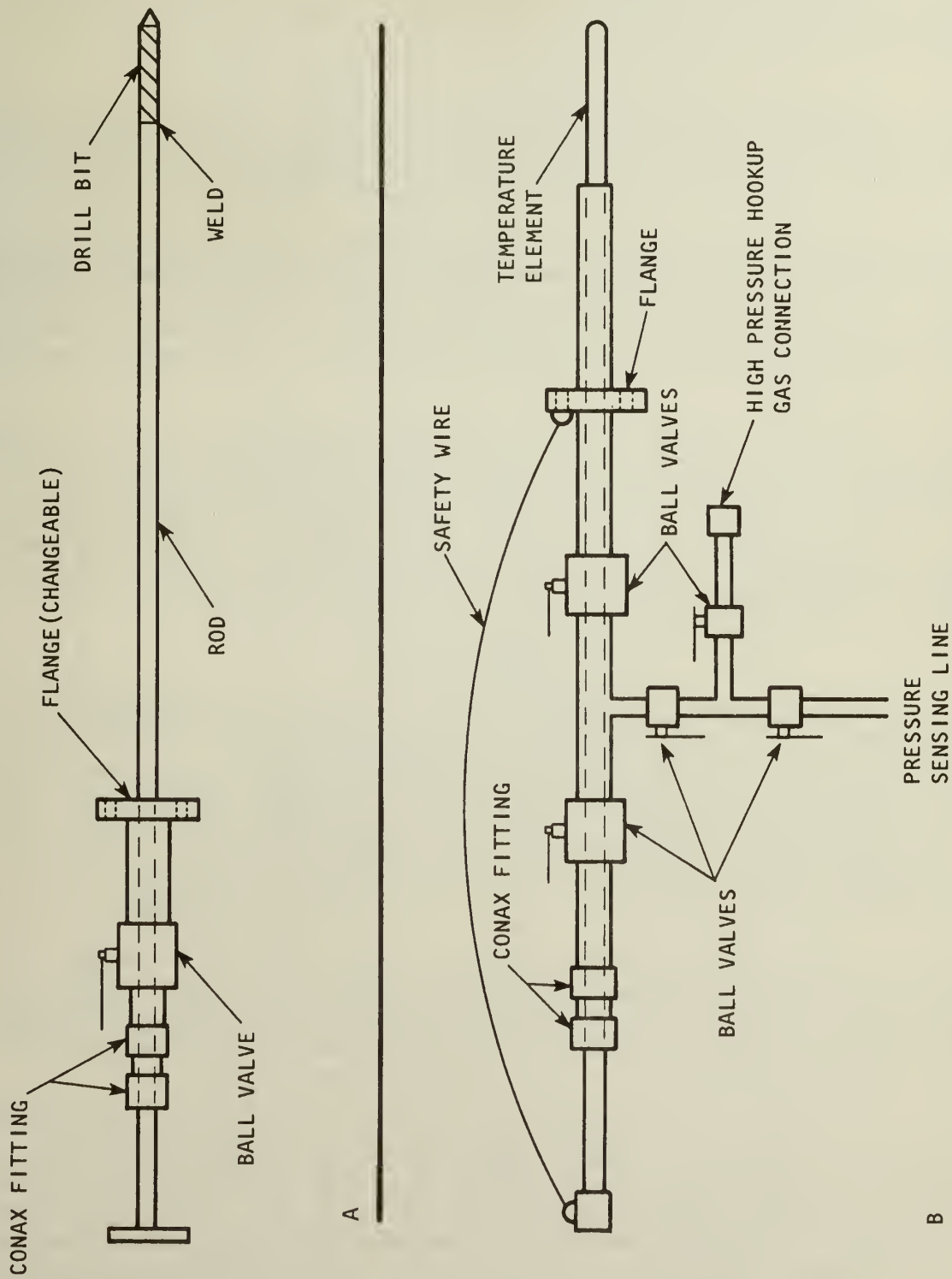


Figure 11-16. ROD-OUT DEVICE AND SIDE-ENTRY PRESSURE PROBE WITH THERMOCOUPLE

11.6 ROLLER MILL

A lignite-derived char was the first material to be ground and dried on a regular basis at the pilot plant facility. The first results were less than satisfactory: The production of fines was excessive. Two of the four grinding journals were removed from the mill. The fines rate was reduced but still was not satisfactory. Tests were run with the two journals removed and the remaining two journals tied back so as to have a small (1/4-inch) clearance between them and the mill bull ring. This arrangement proved satisfactory for the grinding of char.

When the system was used to grind lignite at advanced rates, however, the mill throughput rate was not large enough to keep up with feed rate demands. The two journals were then untied to increase the lignite grinding output at the expense of the char grinding product stream rate.

At this point, a Sweco screen was installed whereby the fines could be separated and the oversize could be recycled. Product stream rate became the important factor. To keep a good product rate and attempt to reduce fines production, the velocity of the mill (RPM of journals) was reduced by about 50 percent to 56 RPM. This proved satisfactory for a particular lignite under a particular set of conditions.

Due to the use of outside storage, the surface moisture level and the physical characteristics of the lignite varied, causing the grinding conditions to vary also. To increase the throughput of coal without plugging the mill, it was decided to return the mill speed to the original rate of 102 RPM and install an adjustable turnbuckle-type journal tie-back. This final setup proved satisfactory and required a minimum amount of changeover time for different types of raw feedstock under changing conditions.

11.7 ZINC OXIDE UNIT

The first experience with hydrogen sulfide corrosion in the process gas heater tubes resulted in a plant shutdown during Run 13A. The unexpectedly high corrosion rate experienced in the gasifier recycle gas system, particularly in the heater tubes of the gasifier recycle gas heater, B-201-1A, was attributed to high concentrations of hydrogen sulfide in the recycle gas. The hydrogen sulfide attacked the Incoloy 800 metal of the tubes, forming an iron-nickel sulfide compound that was liquid at heater-tube temperatures. The material then deposited as a solid in the downstream piping.

In June, 1973, the decision was made that a hydrogen sulfide removal system would have to be employed on the gasifier recycle gas stream. The zinc oxide process was selected after comparing it with alternative processes. Since the materials of construction were long-delivery items, the project was not finished until December of 1973.

The system comprises two packed towers, zinc oxide desulfurizers D-204 A and B, in series. After about a week's operation, the zinc oxide in the lead tower is converted to zinc sulfide. When the hydrogen sulfide concentration in the gas between towers reaches about 10 parts per million, the lead tower is taken out of service. The zinc oxide bed is replaced with fresh material and the freshly charged vessel is put back in service as the second tower in the series. Operation of the zinc oxide system proved entirely satisfactory during subsequent runs. Corrosion of heater tubes was dramatically reduced, and deposits of iron-nickel sulfide compounds in piping downstream of the heaters was eliminated. A flow sketch of the zinc oxide unit is shown as Figure 11-17.

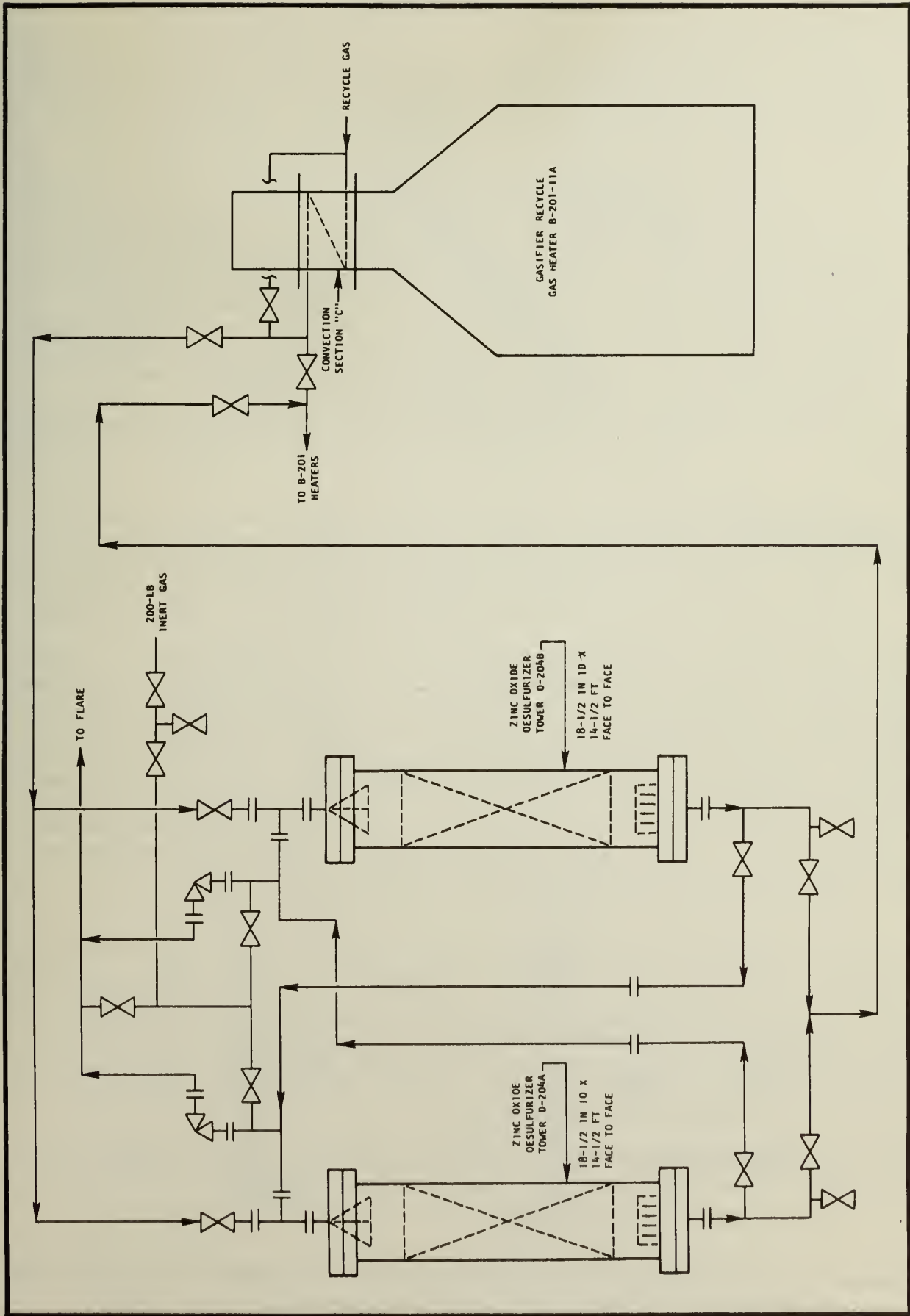


Figure 11-17. ZINC OXIDE DESULFURIZER SYSTEM

11.8 CHAR WITHDRAWAL SYSTEM

The char withdrawal system, comprising char removal hoppers F-215 and F-216, was placed in service during Run 22A in September, 1974. The new lockhopper system was used for several runs as a means of controlling the buildup of intermediate fines material in the gasifier char bed. Intermediate fines or "junk" are materials in the 20 x 65 Tyler mesh range which tend to accumulate in the gasifier char bed. The intermediate fines, which also include attrited acceptor particles, are primarily composed of sand (silica) and clay particles which enter the system with the coal or lignite feedstock. Particles smaller than 20 mesh do not readily shower with the recarbonated acceptor and, therefore, cannot be removed from the system with the acceptor. Intermediate fines which are transferred to the regenerator with the fuel char were recirculated back to the gasifier with the calcined acceptor, because the regenerator fluidizing velocity is not sufficient to strip the intermediate fines from the calcined acceptor inventory. The buildup of intermediate fines was responsible for high gasifier char bed densities. If the density of the char bed approaches that of the acceptor in the gasifier boot, showering of acceptor from the char bed stops, the char acceptor interface is lost, and acceptor circulation stops. Plant shutdown is the final result.

The char withdrawal approach was conceived as a way to remove some of the intermediate fines that accumulated in the char bed from the gasifier. By continually drawing off a slipstream of char from the bed, it was hoped that enough of the "junk" could be withdrawn to compensate for the continual influx of acceptor fines and silica in the fresh acceptor and lignite feeds.

The char withdrawal hoppers, F-215 and F-216, were initially parallel vessels which were attached to transfer line CO-202 which carries fuel char from the gasifier to the regenerator. (See Figure 11-18.) A butterfly valve was used to control char withdrawal rate, and ball valves were used to block in the individual hoppers as they required dumping. Although the setup was relatively simple, pressure upsets were caused in transfer line CO-202 while individual hoppers were being isolated from or put back into the system. These pressure fluctuations invariably upset char transfer to the regenerator, and the char transfer upsets, in turn, upset the entire system. Operating procedures and instrumentation changes were made in an attempt to eliminate the pressure fluctuations, but the char transfer upsets persisted.

To improve the stability of the char transfer system, the parallel char removal system was changed to a series system in Run 26 (see Figure 11-19). In the series system, the lockhopper receiving char directly from the standleg is continuously onstream, so that switching between lockhoppers is avoided. In addition, an automatic purge and vent system was installed so that the pressure drop, dP-2102, across the sloped standleg would remain constant. Gas would be purged into the lockhoppers when the dP-2102 pressure drop was low. The lockhoppers would be vented if the pressure drop was too high.

The series system proved to be an improvement over the parallel system. Char transfer was more stable and upsets occurred less frequently.

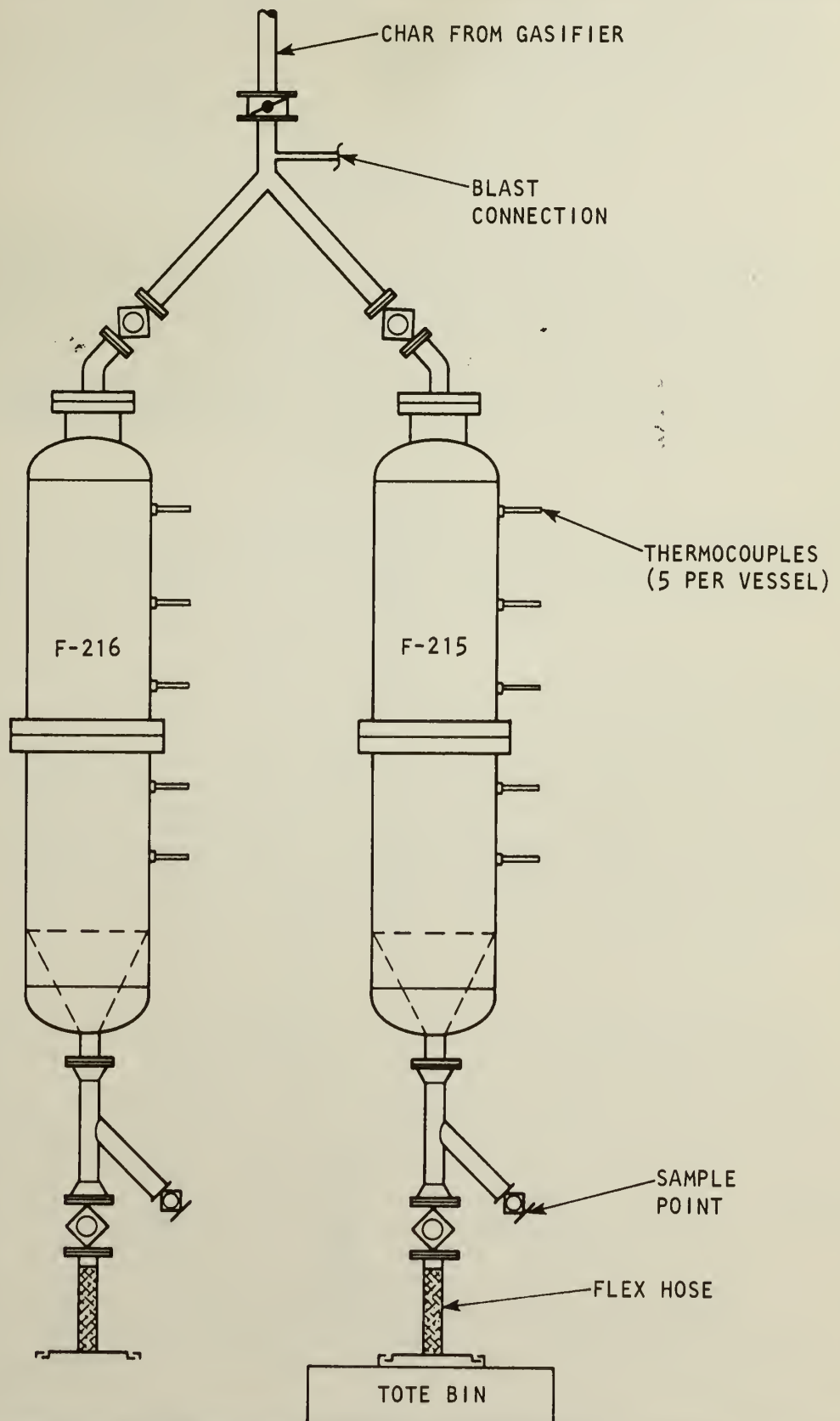


Figure 11-18. CHAR REMOVAL VESSELS F-215 AND F-216 IN PARALLEL

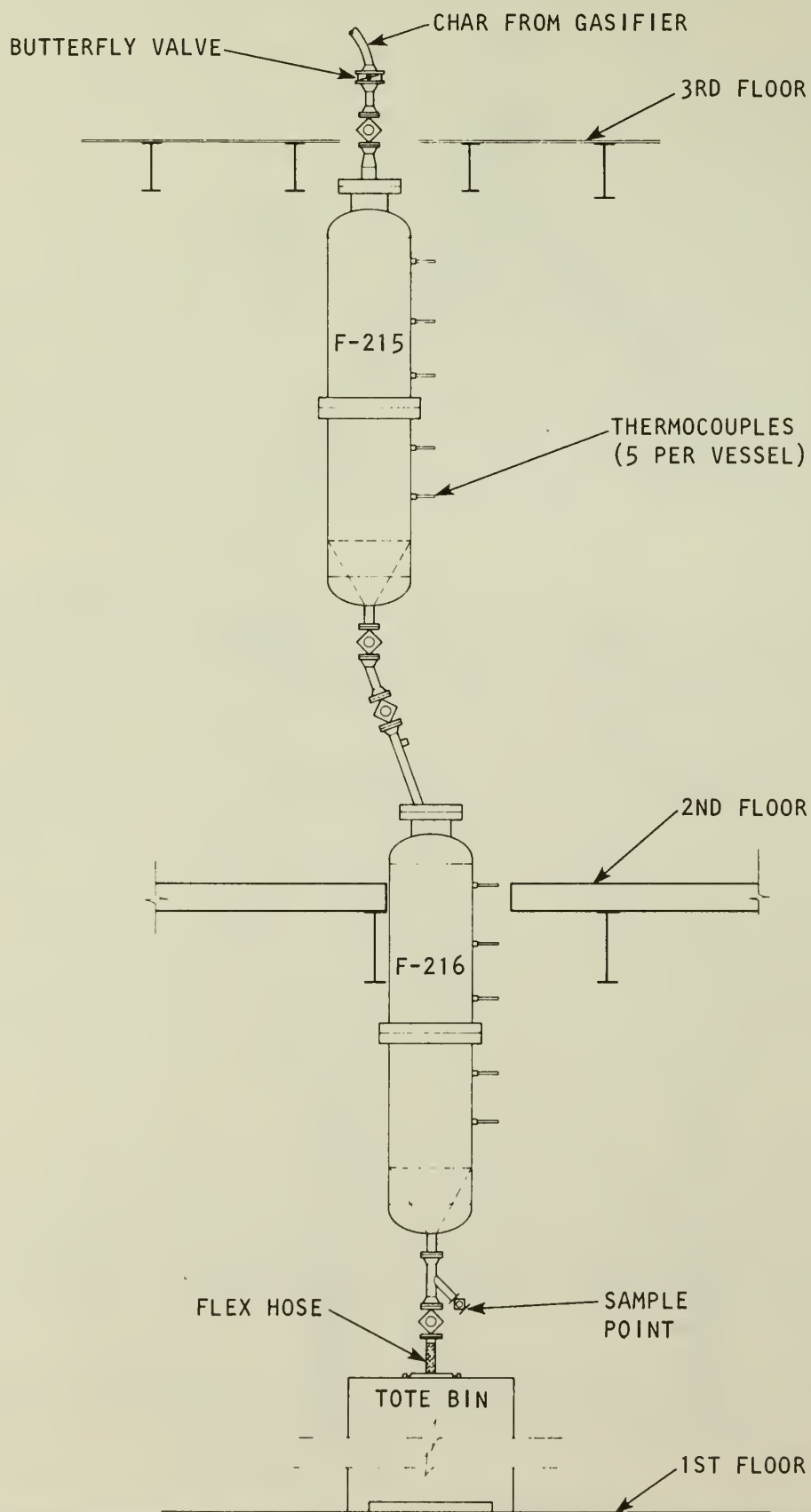


Figure 11-19. CHAR REMOVAL VESSELS F-215 AND F-216 IN SERIES

The char removal system was installed in the pilot plant as an expedient solution to the problem of the buildup of intermediate fines in the gasifier char bed. The char removal system was taken out of service prior to Run 33 when a better method (F-228 spent acceptor removal system - refer to Section 2, Book 1) was devised for controlling intermediate fines accumulation in the gasifier. An acceptor withdrawal system, similar to that of the F-228 system was designed for the commercial plant so the char removal system would not be incorporated into a commercial plant.

11.9 EXTERNAL CYCLONES

Gas cyclones to remove entrained solids from reactor overhead gases were used since the initial startup of the CO₂ Acceptor Pilot Plant. Initially, an external cyclone in the regenerator overhead line removed ash from the regenerator flue gas, and an internal cyclone in the gasifier removed char from the gasifier overhead gases before they left the reactor. The ash removed by the regenerator external cyclone, L-202, was retained in lockhoppers prior to being dumped from the system. The char removed by the gasifier internal cyclone, L-211, simply fell back into the gasifier through a solids dip leg.

During early runs, solids in the flue gas from the regenerator and product gas from the gasifier agglomerated when contacted with water in piping downstream of the gas cyclones, indicating a need for more complete solids removal. The gasifier external cyclone (product gas cyclone, L-222) and second regenerator external cyclone, L-202A, were installed for this purpose.

The second ash removal cyclone, L-202A, installed in the regenerator flue gas line, was put into service prior to Run 22B in November, 1974. Cyclone L-202A was designed according to a procedure from Perry's Chemical Engineers Handbook and was installed downstream in series with the existing cyclone, L-202. (See Figure 11-20.) Addition of the second cyclone substantially reduced the volume of ash fines received by the regenerator quench system. Reduced fines concentration in the regenerator flue gas, coupled with chemical treatment of the regenerator quench water, successfully eliminated plugging problems downstream of the cyclones. The installation of the second cyclone also made the regenerator off-gas acceptable for gas turbine power recovery tests which were conducted later.

The gasifier external cyclone (product gas cyclone, L-222) was installed prior to Run 31 in December, 1975, to remove entrained char fines that escaped the gasifier internal cyclone and were carried to the inlet of the gasifier quench tower, E-301, where deposits formed at the quench tower inlet line and later in the inlet venturi. (See Figure 11-21.) Char dust which was separated from the product gas by the external cyclone fell into the gasifier cyclone accumulator, F-227; it then fell into the gasifier cyclone lockhopper, F-319, which could be isolated and dumped to tote bins at atmospheric pressure. Although addition of the L-222 external gasifier cyclone did not completely eliminate fines agglomeration at the quench tower inlet venturi (gasifier overhead venturi scrubber, L-317), it greatly reduced the severity of the problem. The fines collected in the F-319 lockhopper under the L-222 cyclone also reduced the solids loading in the gasifier quench tower and provided a means to measure the pounds per hour of ungasified char leaving the gasifier through the overhead line.

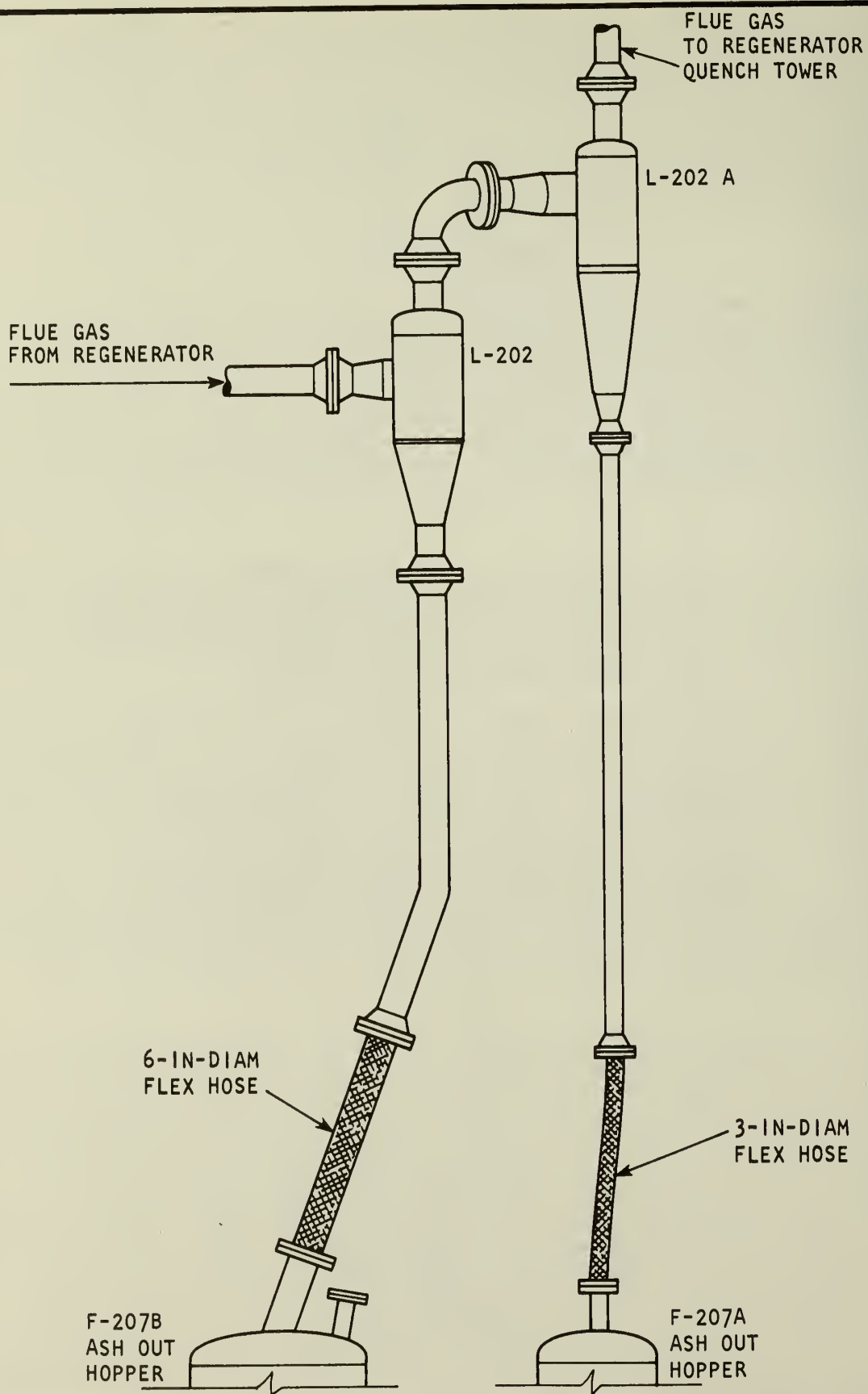


Figure 11-20. REGENERATOR EXTERNAL GAS CYCLONES

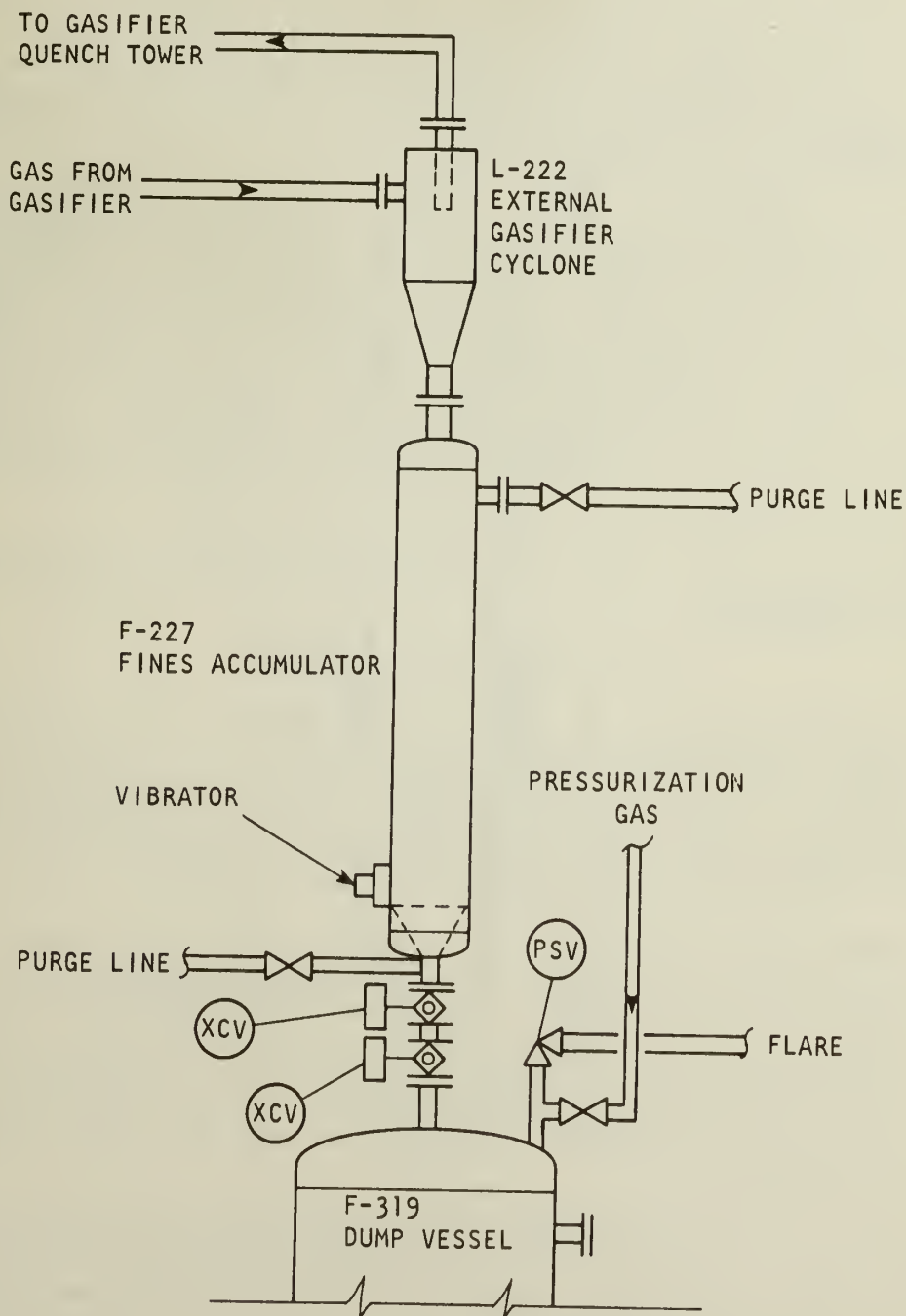


Figure 11-21. GASIFIER EXTERNAL GAS CYCLONE

Through Run 14B in November, 1973, the engager pot, F-222, had the configuration detailed in Figure 11-22. The conveying gas enters the bottom and lifts the solids up the center pipe (acceptor lift line) to the regenerator, which is approximately 100 feet above the engager pot. This design was suspected of causing acceptor attrition at the point where solids enter the lift line.

During the shutdown which followed Run 14B, the engager pot was modified as shown in Figure 11-23. The recarbonated acceptor from the gasifier entered the lift line by means of a slip joint. Fresh makeup entered the same lift line a few feet up from the return line by a similar slip joint arrangement. A sleeve was installed in the bottom gas inlet nozzle which then projected into the lower end of the lift line.

After Run 16, the engager pot was opened for inspection. Severe erosion was discovered in the lift line both where the 4-inch acceptor return and the 2-inch fresh makeup entered the line. The engager pot was modified again, as shown in Figure 11-24, in an attempt to eliminate the erosion. The modification was similar to the original engager pot design, but with the acceptor lift line shorter so that it did not extend into the pot as far. Originally the line extended to within 4 inches of the bottom of the engager pot. As modified, it extends to within about 1 foot of the bottom. This extra distance allows the presence of a fluidized bed, which significantly reduces attrition and eliminates erosion in the engager pot.

The engager pot design remained the same from the Run 16 modification to the end of the project.

11.11 FINES DISPOSAL SYSTEM

The coal grinding section of the CO₂ Acceptor Pilot Plant, like any operation which involves grinding solids to a specific size distribution, produces unwanted fines. Since onsite reclamation of fines is not feasible, coal fines are discarded. Fines are mixed with water and transported as a slurry to the waste disposal pond. This method has proved to be the cleanest, safest, and most efficient way to dispose of the unwanted fines.

During early runs, fines which were dumped from the lignite fines storage bin, F-104, in the 100 Area structure went into tote bins and were then dumped manually into a gondola truck. The fines which were discharged from the Sweco lignite feed screen, L-157, on the tenth floor usually went directly to the gondola truck, although they could be routed to tote bins if necessary. With this system dust conditions were generally quite severe, and smoldering, spontaneous fines fires were not uncommon. The need for a cleaner, safer, fines disposal system was apparent.

The weakest link in the original fines disposal system was the gondola truck. In order to fill the truck, fines became mixed with fresh air which created excessive amounts of dust and ideal conditions for spontaneous combustion. The lignite fines dump hopper, F-521, was constructed to replace the gondola truck. The F-521 hopper is a simple rectangular metal vessel with a tapered bottom. It is equipped with water showering devices and an eductor type slurry withdrawal. The lignite fines hopper discharges to the waste disposal pond and is supplied with water for the showering devices and the slurry withdrawal inductor from the same pond. F-521 receives material from Tote bins through an opening in its top. A sketch of F-521 is included as Figure 11-25.

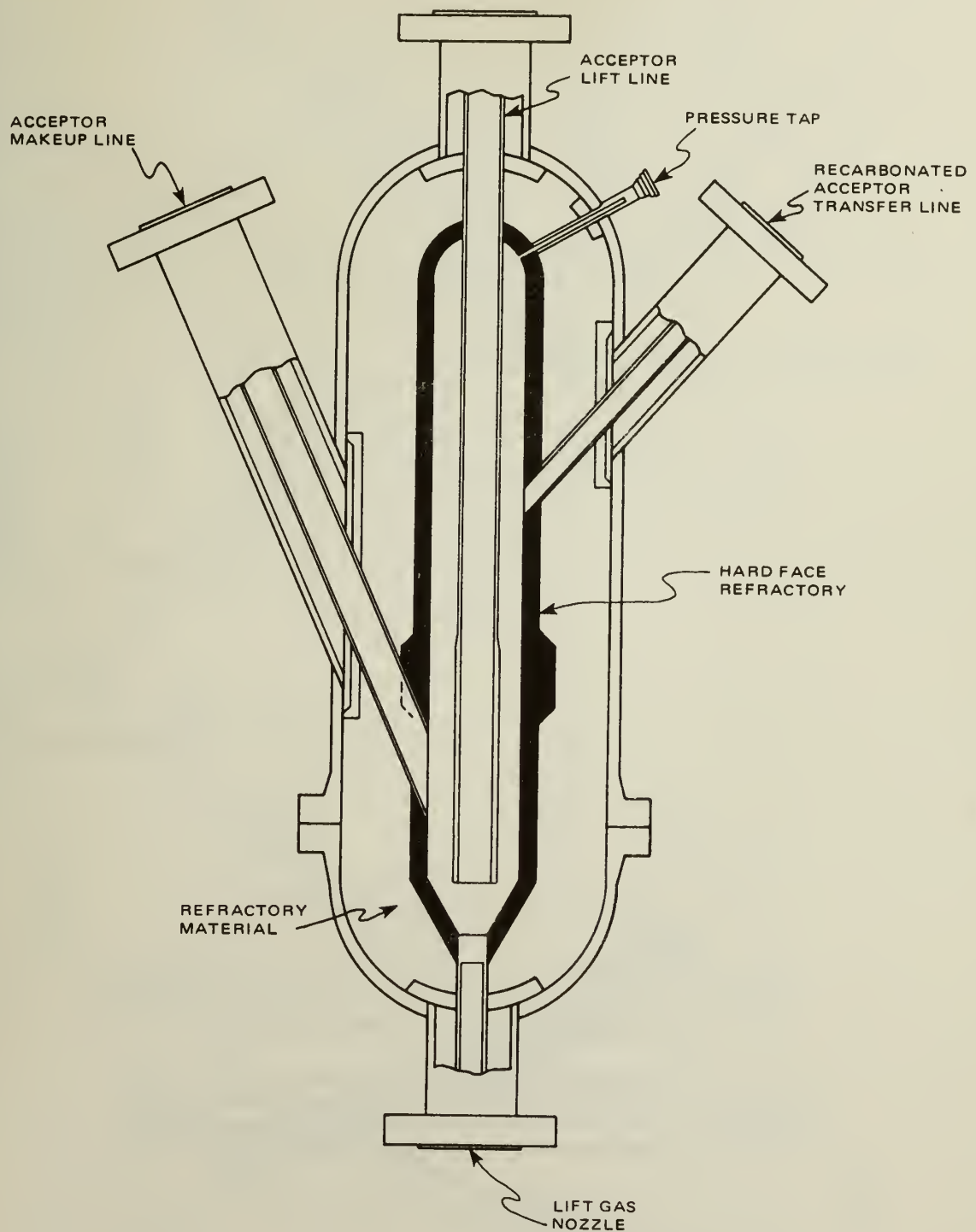


Figure 11-22. F-222 ENGAGER POT ORIGINAL DESIGN

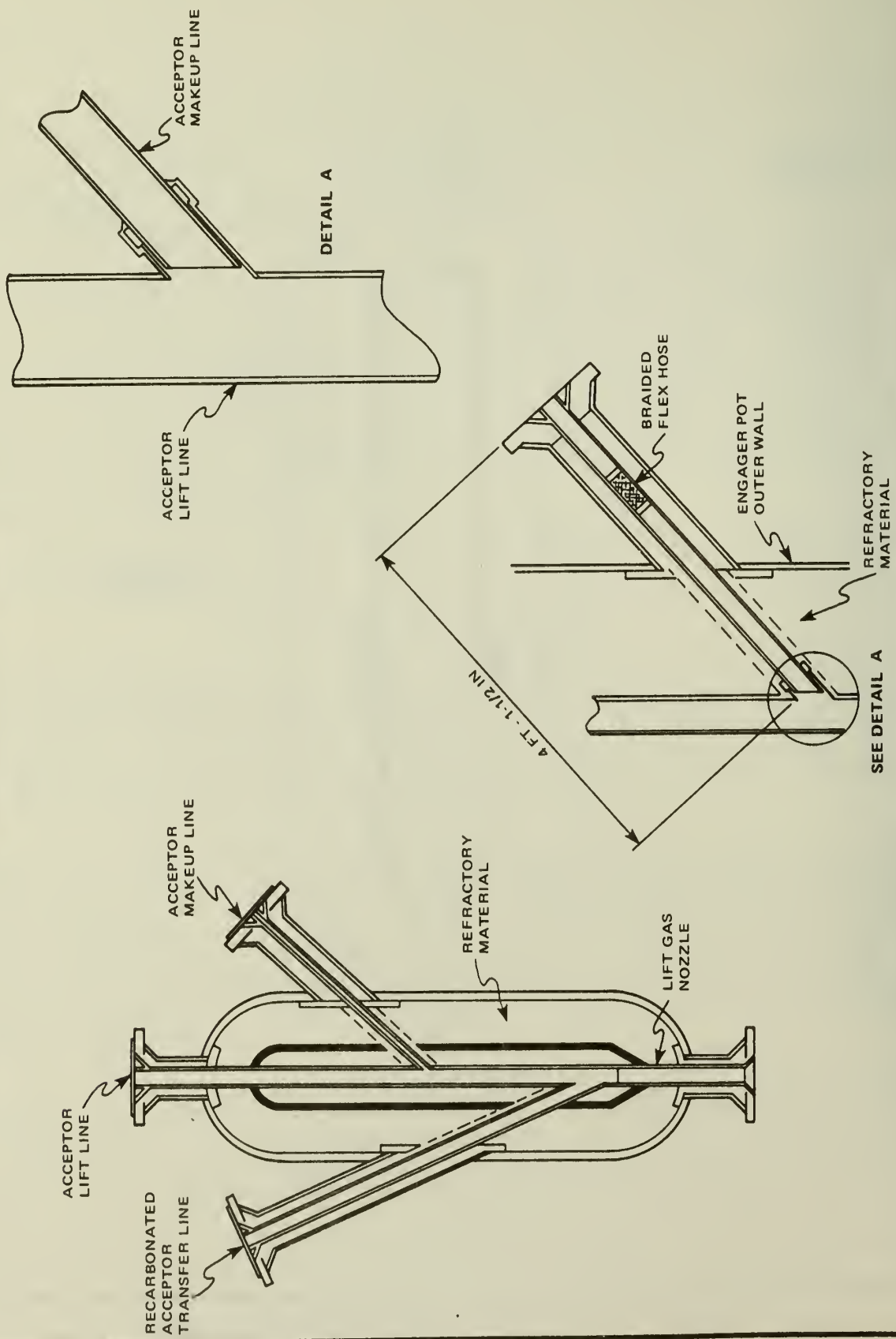


Figure 11-23. ENGAGER POT MODIFIED DESIGN

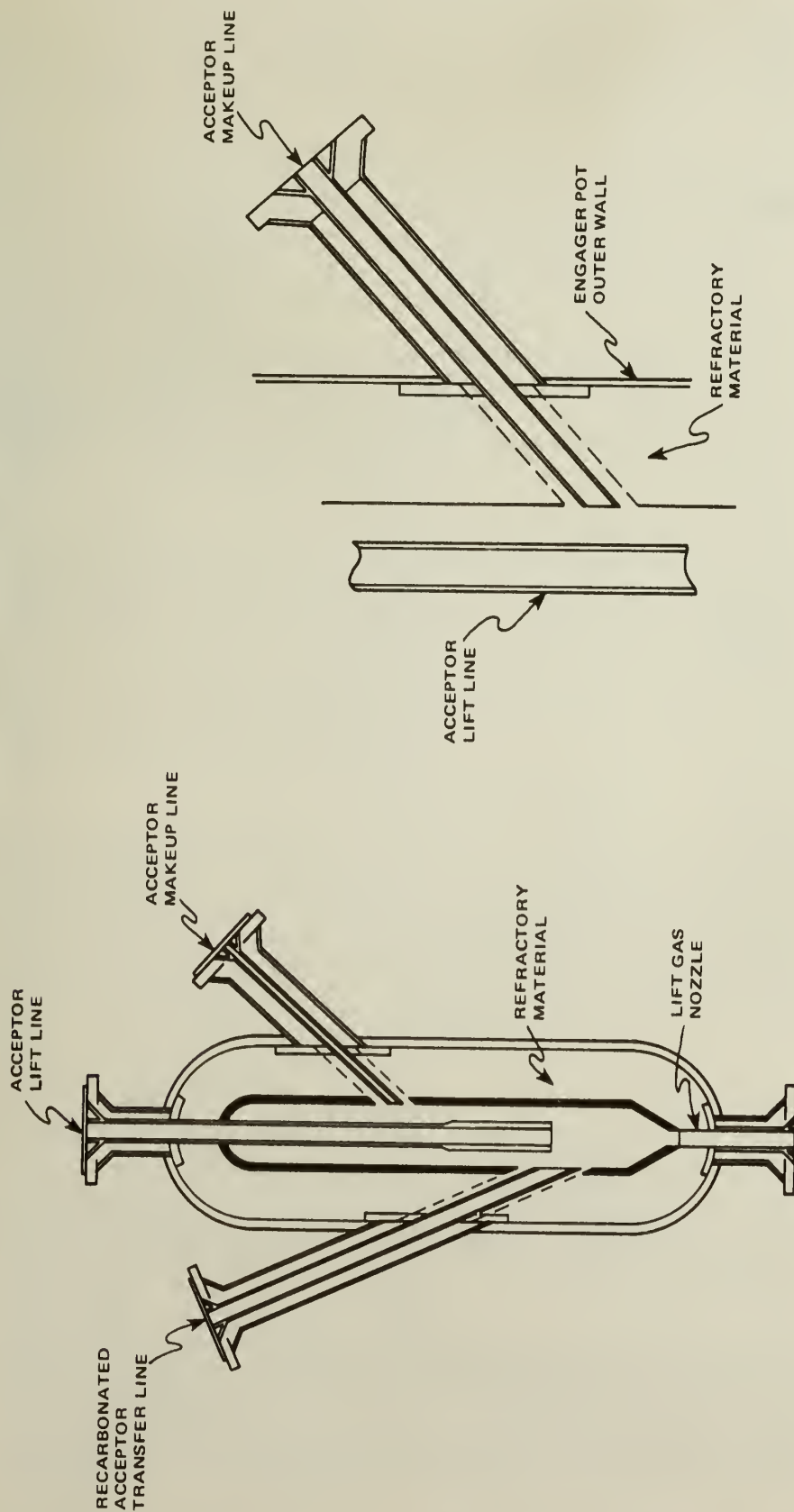


Figure 11-24. ENGAGER POT FINAL DESIGN

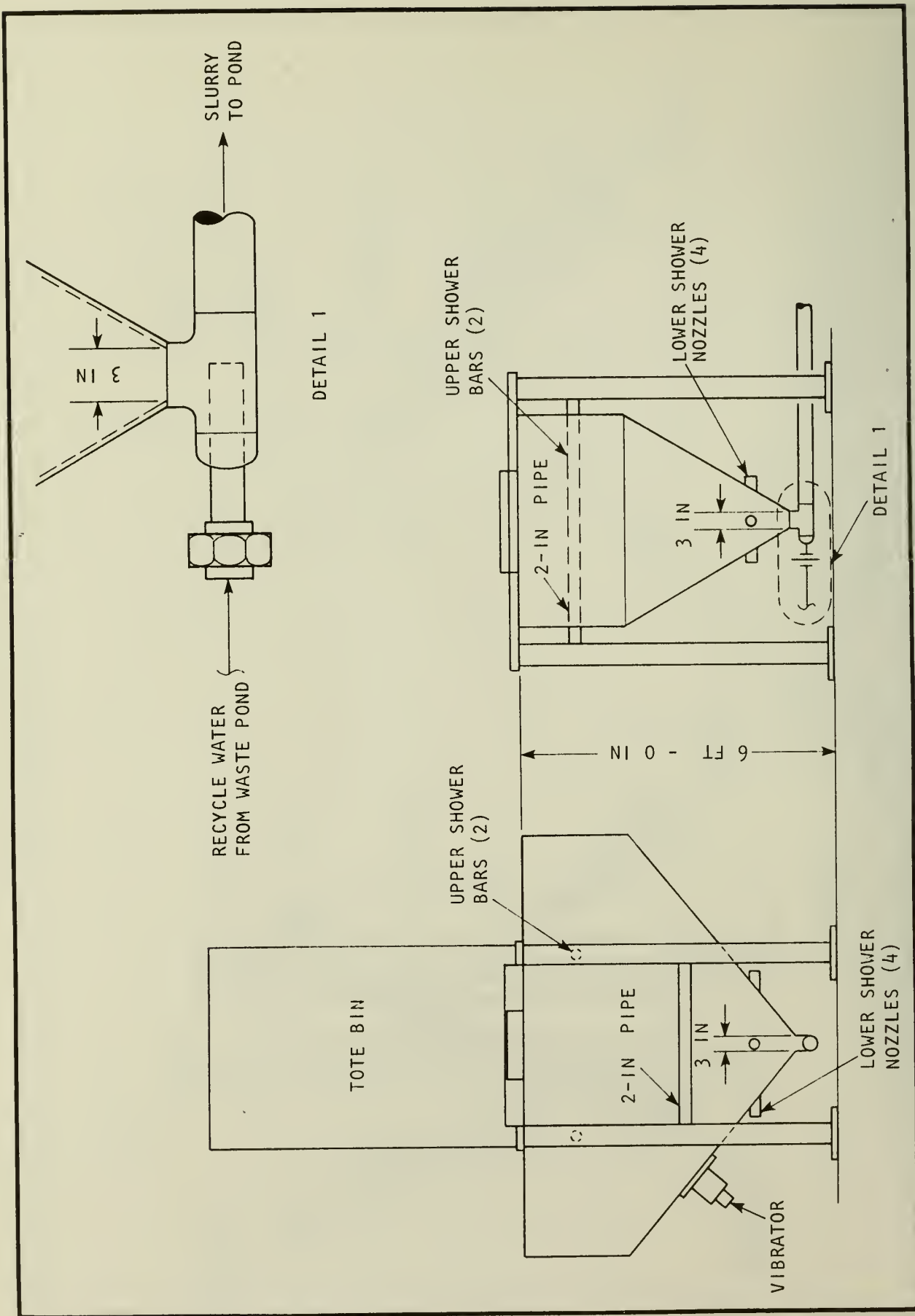


Figure 11-25. F-521 LIGNITE FINES DUMP HOPPER

Although the lignite fines dump hopper eliminated the bulk inventory of fines onsite in the gondola truck, dust conditions associated with handling fines in Tote bins remained. The lignite fines disposal system, as depicted in Figure 11-26, was constructed and installed during the summer of 1975 to eliminate manual fines handling in the grinding area.

A lignite fines dump vessel, F-105, was installed at the old Tote bin station under the F-104 lignite fines bin in the 100 Area structure, and a lignite fines slurry tank, F-106, was placed in the 200 Area structure to receive the fines from the Sweco screen on the tenth floor. Parallel pumps, J-524 A and B, were installed at the waste disposal pond to provide the water necessary to the dump vessel and slurry tank, which in turn discharged back to the pond.

Fines disposal via F-105, the dump vessel in the 100 Area structure, is a batch process. Fines which accumulate in the F-104 fines storage bin are dumped directly to F-105. In F-105, the fines are mixed with water and the vessel is pressurized to 18.5 psig with inert gas. The slurry in F-105 is then removed from the vessel by a water eductor to the waste disposal pond.

The F-106 lignite fines slurry tank, which receives fines from the Sweco screen on the tenth floor, is a smaller version of the F-521 lignite fines dump hopper. When in operation, it continually receives fines, showers them with water, and discharges them to the waste disposal pond via a water eductor. A sketch of the F-106 lignite fines slurry tank is shown in Figure 11-27.

The fines disposal system modifications made fines disposal considerably cleaner, safer, and less time consuming.

11.12 CONTINUOUS FEED SYSTEMS

Steady-state operation of a continuous process requires uninterrupted feed of raw materials to the process. When the raw materials are gases or liquids, compressor and pumps effectively bring the materials to system pressure or above--allowing uncomplicated continuous feed. However, uninterrupted makeup of solids is slightly more difficult. Two solids lockhopper systems, described in this subsection, were used at the CO₂ Acceptor Pilot Plant to provide continuous feed.

11.12.1 LIGNITE LOCKHOPPERS

The lignite lockhopper system was designed to feed lignite or char to the process. This system is of particular interest, since (1) it is semi-automatic as opposed to the other lockhopper systems (acceptor makeup, acceptor withdrawal, and ash lockhoppers), which are manual, and (2) its operation allows continuous feed of lignite or char to the system.

During the initial runs, lockhopper feed could not be maintained. Line plugs between the lockhoppers and the gasifier often occurred. Apparently, the inability of the lockhopper purge gas systems to supply enough gas to make up for leaks and replace the bed solids volume caused most of the problems. The following modifications were made to the lockhopper system:

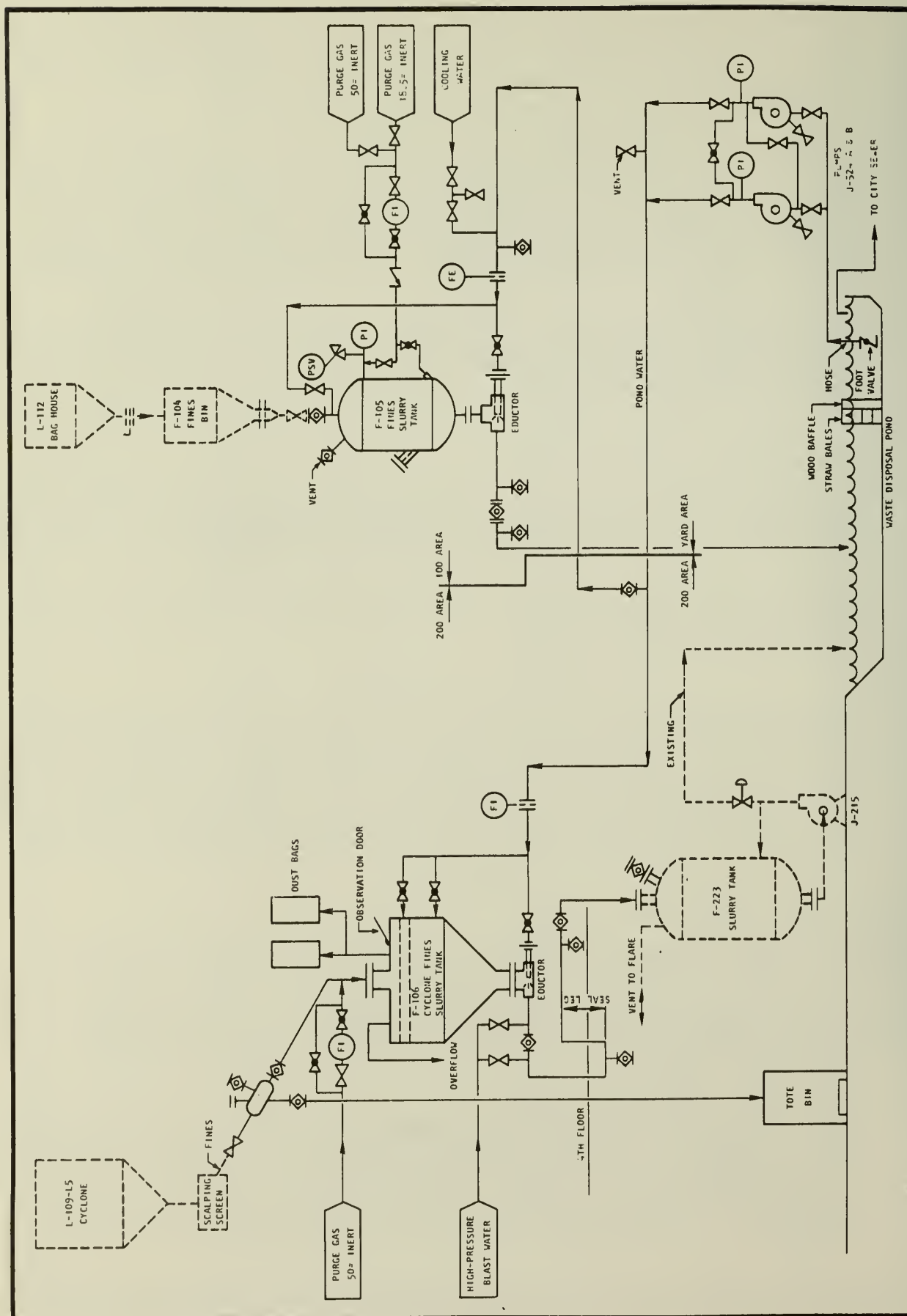


Figure 11-26. LIGNITE FINES DISPOSAL SYSTEM

- (1) The use of rotameters to supply the system makeup purges was abandoned in favor of an automatic system using differential pressure control valves.
- (2) The purge gas rate down the lockhopper feed line to the gasifier was increased from 250 SCFH to about 2000 SCFH.

Figure 11-28 represents the lockhopper system as it now exists. Since both halves of the system are identical, and for the sake of clarity, only one lockhopper is shown. The functioning of the equipment during all modes of operation (filling, pressuring, feeding, and depressuring) is given below:

Sequence of Operation

Positioning or Action

<u>Operation</u>	<u>Feeder</u>	<u>XCV-4</u>	<u>dPCV-6</u>	<u>dPCV-8</u>	<u>XCV-9</u>	<u>XCV-10</u>	<u>XCV-14</u>
Filling	Off	Closed	Closed	Modulating	Closed	Open	Open
Pressuring	Off	Closed	Closed	Modulating	Open	Closed	Closed
Feeding	On	Open	Modulating	Modulating	Closed	Closed	Closed
Depressuring	Off	Closed	Closed	Modulating	Closed	Closed	Open

During filling, preheated lignite or char is fed into the hopper through XCV-10; valves XCV-4, dPCV-6, and XCV-9 are closed. Valve XCV-14 remains open to allow gas displacement as solids fill the hopper. The weigh cell recorder, WR-12, registers the amount of solids fed. When the operator has determined that the hopper is full, feeding is stopped in preparation for pressuring. Pressuring consists of closing valves XCV-10 and XCV-14 and opening valve XCV-9 fully. The restriction orifice, RO-7, allows the hopper to be pressured at a rate which will not drop the purge header pressure.

When dPT-3 indicates that the hopper pressure is 1 psi greater than the system pressure, XCV-9 closes and dPCV-6 starts modulating. The system is now ready to feed.

The replacement of the original purge rotameter with dPCV-6 greatly improved the lockhopper operation. This valve automatically compensates for small leaks and for the increased gas volume required due to solids feed from the hopper. Valve dPCV-8 controls a constant differential pressure across dPCV-6 to ensure that the valve operating characteristics remain constant.

To feed from the hopper, valve XCV-4 is opened and the feeder started. When the weigh recorders indicate that the hopper is empty, the feeder is stopped. Valve XCV-4 remains open for an additional 30 seconds to allow any solids above it to feed into the gasifier. This practice had improved valve operation by eliminating much of the seat damage caused when the valve was closed with solids in it.

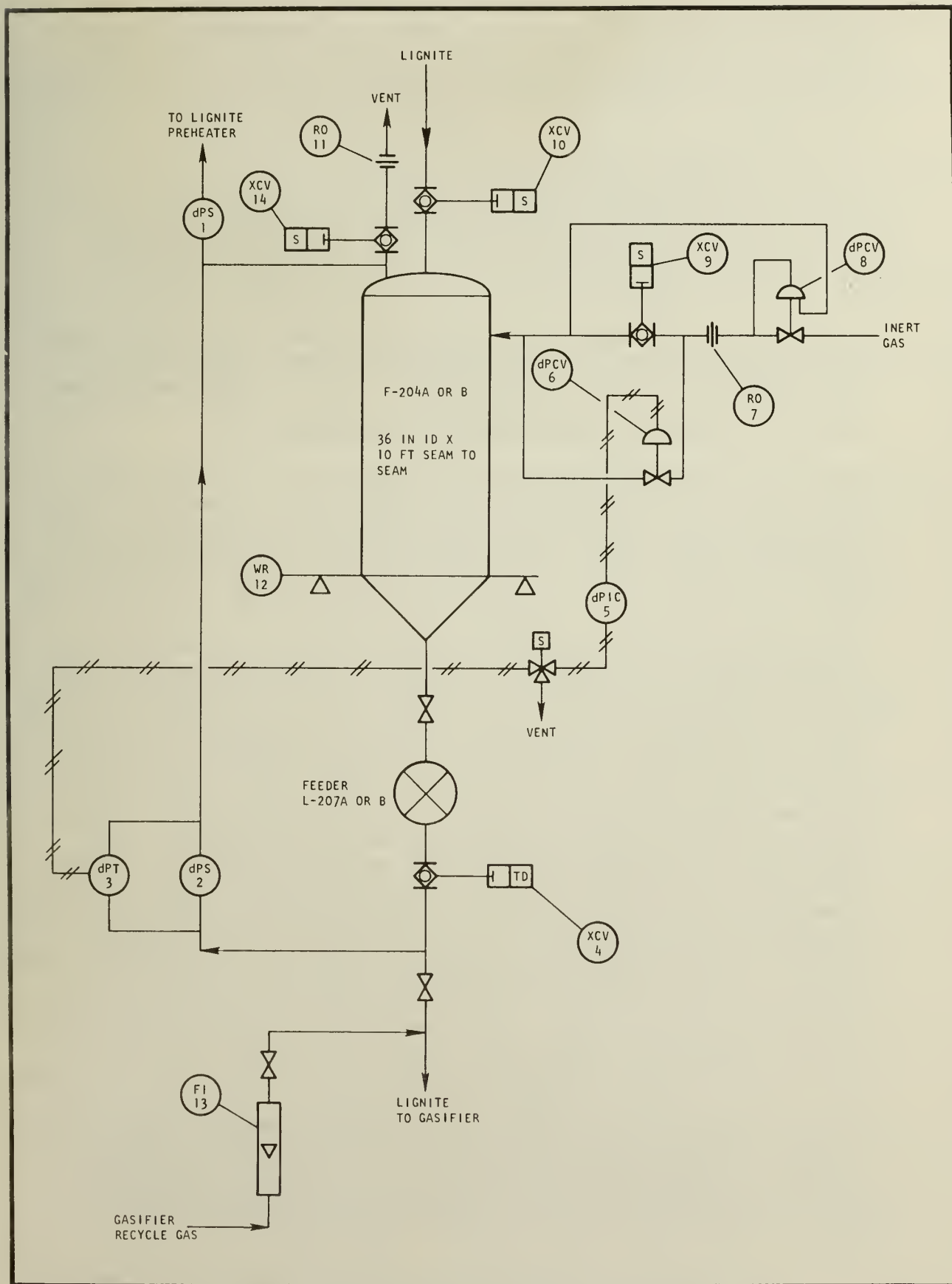


Figure 11-28. LIGNITE LOCKHOPPER SYSTEM

To depressure the hopper, dPCV-6 is closed and XCV-14 opened. The downstream restriction orifice, RO-11, allows the lockhopper to be depressured at a controlled rate. When dPS 1 indicates that the lockhopper pressure is 1 psi greater than the preheater pressure, XCV-10 is opened; the hopper can now be filled by starting the feeder from the preheater (not shown.)

Below valve XCV-4, a gasifier recycle gas purge has been supplied to (1) help move solids through the line to the gasifier and (2) to keep gasifier steam from entering the line. Without this purge, steam condensation in the lignite feed line would cause plugging problems.

11.12.2 SERIES LOCKHOPPER FEED SYSTEM

The second type of solids feed system used in the auxiliary fuel system, F-226 A and B, and the fresh acceptor feed system, F-206 A and B, is the lockhoppers-in-series configuration. Since the auxiliary fuel and fresh dolomite feed systems both operate in the same manner, only the auxiliary fuel system is described in this subsection.

The auxiliary char feed system was installed prior to Run 26 in May, 1975, to provide an alternate source of fuel to the regenerator in the case of an upset in the char fuel transfer from the gasifier. In this system, the rotary feeder, L-209, runs continually, feeding from the lower char hopper, F-226B. Its speed may be varied from the main control room.

The system operation is as follows; starting with an empty system and the feeder off. The hoppers are isolated from the main system by means of a valve under the bottom hopper, F-226B. The bottom hopper is filled from a tote bin by dropping the solids through the top hopper and the open valve between the two hoppers. The bottom hopper has two level indicators (Dynatrols), one located in the lower portion of the vessel and one in the upper portion of the vessel. These are connected to two alarm lights on the alarm panel in the main control room. As the bottom indicator is covered, it becomes satisfied and the low level light on the panel goes off. The charge level continues to rise, satisfying the upper level indicator also. When the bottom vessel is full, determined by its capacity and the known weight of the charged material, the valve between the vessels is closed. The bottom vessel is then pressurized to system pressure, opened to the main system, and the feeder started. When the upper level indicator in "B" hopper lights in the control room, the "A" hopper is charged with one Tote bin of char, coal, or lignite. The "A" hopper is then pressurized to system pressure with the valve between the vessels still closed. When the lower level indicator in "B" hopper lights up, indicating capacity to hold the contents of "A" hopper, the valve between the two vessels is opened. When the charge has been transferred from "A" hopper to "B" hopper and both alarms are again satisfied, the valve between the two vessels is closed. Then "A" hopper is depressurized and made ready to receive another charge of material. In this manner it is possible to maintain a continuous auxiliary char feed while filling the feed hoppers in batches.

In order to maintain smooth flow of char out of the lockhoppers and into the char transfer line, a purge is put into the lockhoppers (Figure 11-29). The differential pressure, dP-2098, between the lower lockhopper and the auxiliary fuel inlet line to the char transfer lift line is used to control the purge, so that the lockhopper pressure is kept higher than that downstream at the inlet line.

A thermocouple in the char lift line, CD-204, indicates whether auxiliary fuel is flowing in the line. Auxiliary fuel is cooler than the char in the lift line, so auxiliary fuel causes a drop in temperature when it enters the lift line. Therefore, whenever auxiliary fuel flow stops a temperature rise is noted on the control room chart recorder. Operators then take appropriate action to re-establish the auxiliary fuel feed.

A sketch of the auxiliary fuel system, F-226 A and B, is shown in Figure 11-29. The fresh acceptor feed system, F-206 A and B, is depicted in Figure 11-30.

11.13 REGENERATOR ACCEPTOR REMOVAL SYSTEM

The regenerator acceptor removal lockhopper, F-228, was installed prior to Run 33A in January, 1976. The purpose of F-228 is to withdraw spent acceptor from the system in order to make room for continuous fresh acceptor makeup. The purged lockhopper, F-213, which had previously performed spent acceptor withdrawal from the gasifier boot, functioned satisfactorily; however, "junk" (acceptor fines and silica particles suspended in the gasifier char bed) was not removed. Since F-228 withdraws acceptor directly from the regenerator acceptor bed, junk which is transferred to the regenerator from the gasifier char bed through the fuel char transfer lines, CO-202 and CO-204, is withdrawn with the spent acceptor. The use of F-228 instead of F-213 made the eventual removal of the char withdrawal system possible.

The F-228 acceptor removal hopper is tied into the regenerator through the old devolatilizer acceptor transfer nozzle which was welded shut when the devolatilizer was abandoned. Calcined acceptor flows by gravity feed from the top of the acceptor bed in the regenerator through a 3-inch stainless steel water-jacketed line, CD-205. A butterfly valve (XCV-2187) in CD-205, which regulates acceptor withdrawal rate, is controlled automatically by the acceptor bed level in the regenerator. Consequently, the more fresh acceptor makeup is added to the regenerator; the more spent acceptor is withdrawn to F-228.

The F-228 regenerator acceptor removal system is shown in Figure 11-31.

11.14 PURGE GAS SYSTEM

Due to the necessity for solids handling on a large scale at the CO₂ Acceptor Process Gasification Pilot Plant, purge gases are necessary to keep solids from collecting in pressure-temperature taps that enter the reactor and solids transfer lines. The original plant design called for three process purge gases ("A" gas, "B" gas, and "C" gas), a nitrogen system, and a high-pressure inert gas system which could also provide

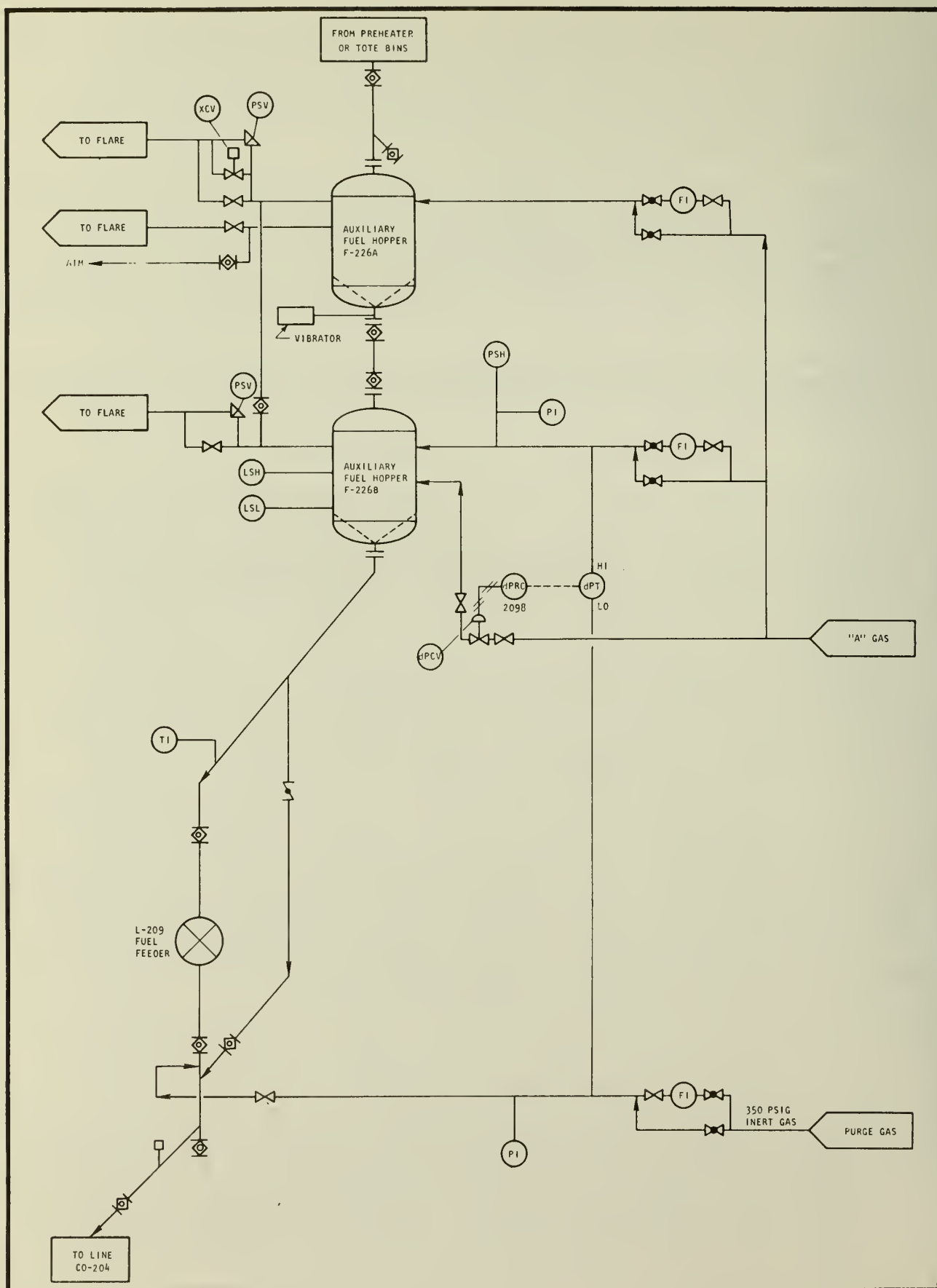


Figure 11-29. F-226A AND B AUXILIARY FUEL SYSTEM

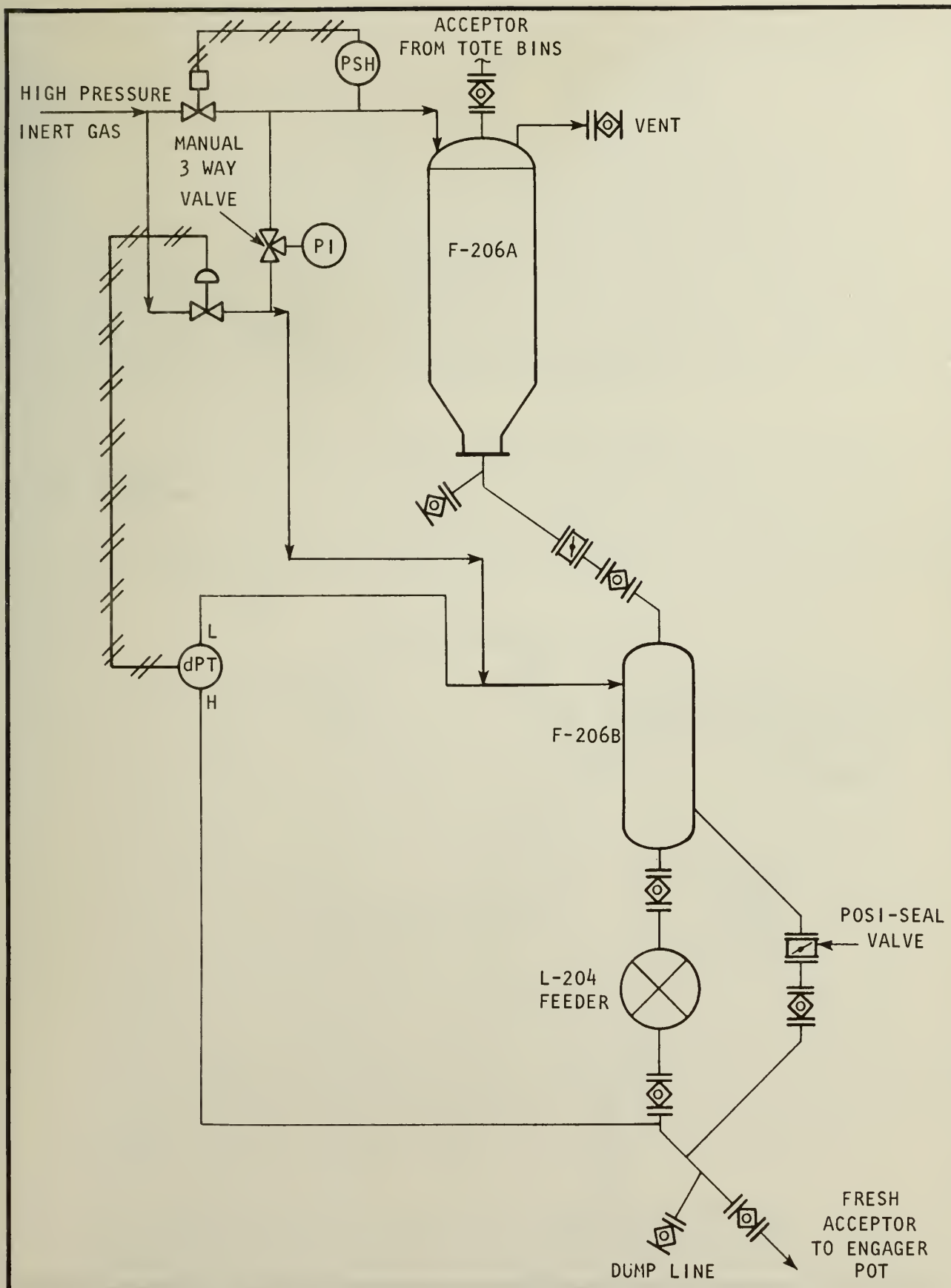


Figure 11-30. F-206A AND B FRESH ACCEPTOR FEED SYSTEM

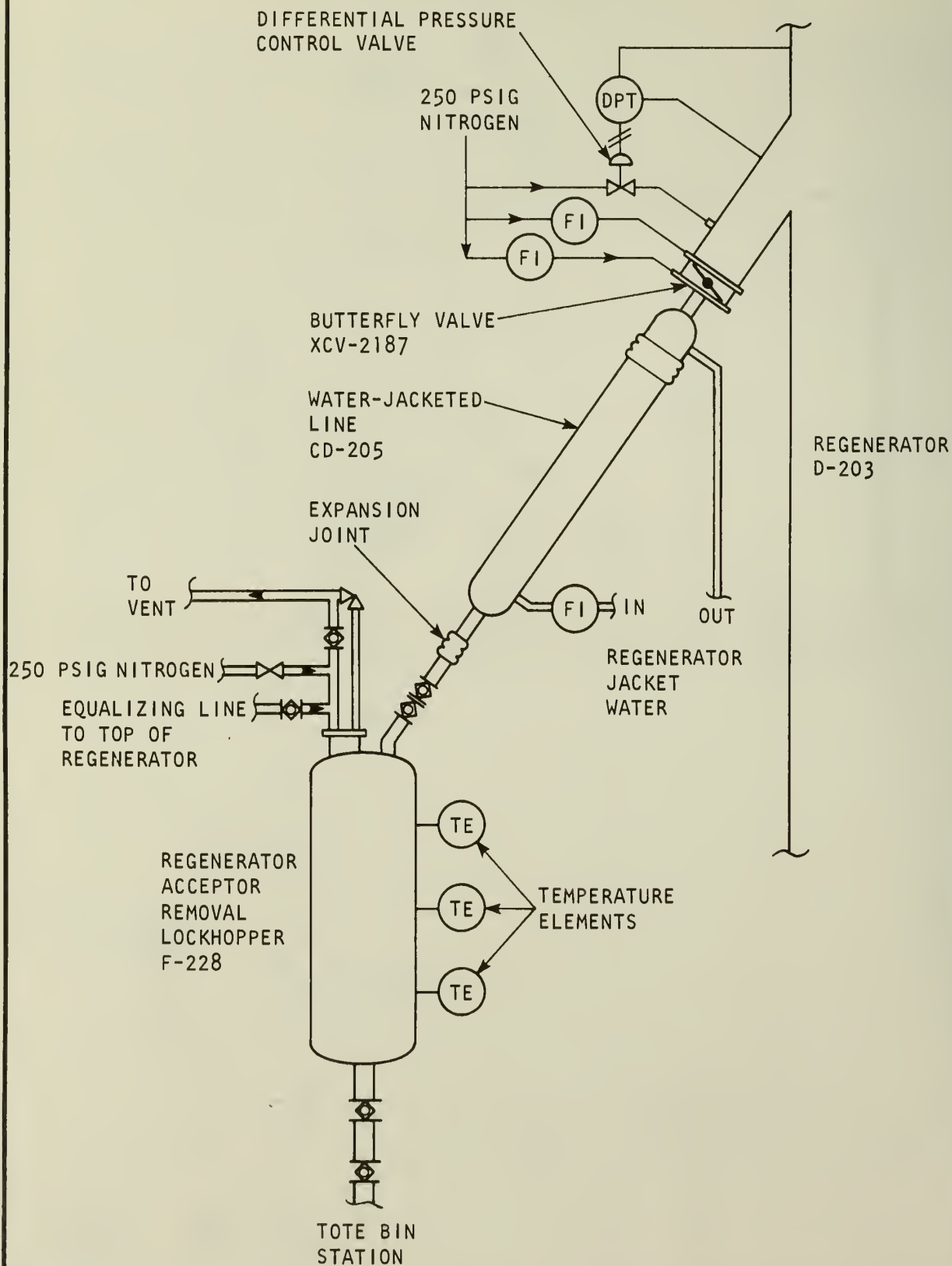


Figure 11-31. F-228 REGENERATOR ACCEPTOR REMOVAL LOCKHOPPER

gases for purging purposes. "A" gas and "B" gas, which are cleaned, compressed, dried overhead gases from the regenerator and gasifier, respectively, have been used to purge their respective system as intended during plant operation.

Originally, CO₂ was to be recovered from the regenerator flue gases and used as "C" gas. Due to the short duration of early runs, the process did not reliably produce enough CO₂ to pressure the "C" gas system. Since high-pressure inert gas had to be substituted to hold "C" gas header pressure, the decision was made to permanently furnish inert gas to the "C" gas header. The hot potassium carbonate system designed to remove CO₂ from the regenerator flue gas (though not used as planned), was kept in service to provide potassium carbonate solution to other systems in the plant. The CO₂ gas compressor, J-309, which was supposed to compress the CO₂ for the "C" gas system, was supplied with low-pressure inert gas and used to furnish lift gas to the char lift line, CO-204.

The nitrogen system, installed before the first run, was intended to supplement the other purge gas systems and the instrument air system when necessary. Later, a nitrogen header was installed in the main structure of the plant to provide pure nitrogen for purging and blast line purposes. The nitrogen system consisted of a liquid nitrogen tank, two cryogenic nitrogen pumps, gas vaporizers, and the necessary valves and controllers.

11.15 STEAM SUPERHEATER

Monitoring and controlling steam to the gasification reactor was a problem encountered early in the project. Original design had 350-psig steam from the utility area piped directly to the process heater, where it was heated to process temperatures and sent to the gasifier. The original setup was workable, but several problems with condensate formation in the 350-psig steam supply line to the process heaters were encountered. The most noticeable result of condensate in the steam line to the process heaters usually materialized immediately after steam was sent to the heaters. As steam entered the 1500°F heater tubes, it carried the condensate in the line with it. The condensate would instantly vaporize and cause a surge of flow to the gasifier. More often than not, the surges in the gasifier would result in major upsets. A more passive, yet equally important, effect of condensate in the 350-psig steam supply line was its effect on steam flow calculation around the orifice. To alleviate the problems of condensate formation ahead of the flow measuring orifice, the 350-psig steam was routed through the unused devolatilizer process heater convection section, B-207-C, where it was superheated before it went to the gasifier process heaters. Reduction of the already near maximum heat load on the gasifier process heaters was also a fringe benefit of superheating the steam in the B-207-C convection section.

The convection section was used as a steam superheater through Run 26B when the decision to superheat the steam with B-207-B heater was made. Experience with the convection section had shown it could only maintain a constant steam temperature near 580°F without causing excessive heater

stack temperatures. By routing the steam to the B-207-B heater to be superheated, higher, more desirable superheated steam temperatures were maintained and less natural gas was used as heater fuel.

11.16 ASH LOCKHOPPER DUMP SYSTEM

During most of the project, ash removed from the regenerator flue gas by the L-202 inline gas cyclones was roughly measured by load cells attached to the ash hoppers, F-207A and F-207B. These hoppers collected the ash from the cyclones. The ash in the F-207 hoppers was then dumped to the spent dolomite/ash slurry tank, F-223, and slurried to the waste disposal pond.

As the project advanced, the heat/material balances became more critical for steady-state operations. A more accurate method was necessary for measuring the amount of ash removed from the regenerator overhead gas than the method of load cells attached to stationary vessels which could not be completely isolated from piping loads. The ash removal hopper, F-207C, was installed directly below F-207A and B for this purpose. A sketch of F-207C is shown in Figure 11-32.

The ash removal hopper, F-207C, is equipped with load cells and is similar to F-207 A and B. However, all piping connected to F-207C can be quickly disconnected, allowing the vessel to be completely suspended by the load cells. This type of arrangement ensures a more accurate weight of the ash in the hopper. After the weight of the ash in the hopper has been determined, the vessel is subjected to slight pressure and the ash is removed from the vessel to the tote bins outside the structure. The material in the tote bins is then weighed on a conventional scale to ensure a correct measurement of ash removal from the system.

11.17 LIGNITE PREHEATER FEEDERS

The original design of the materials handling area used regenerator flue gases to fluidize the lignite preheater, D-101. This use of flue gas presented some operational problems because the flue gas flow to the preheater was withdrawn ahead of the regenerator back-pressure control valve, PCV-2071. During a process upset, the regenerator vent rate could drop below the withdrawal rate of flue gas to the preheater. This would result in depressurization of the system if operators did not take corrective action immediately. The pilot plant was modified to eliminate this system interaction by using steam for preheater fluidization. Since the use of steam in the preheater was not anticipated by the designers of the system, the problem with condensate that collected around the mechanical feeders at the inlet and outlet of the preheater was also not anticipated. The following is a discussion of the modifications associated with the mechanical feeders.

The hot lignite rotary feeder, L-110, which supplied preheated lignite from the lignite preheater to the lignite lockhoppers, F-204 A and B, was the first to demonstrate that condensate from the fluidizing steam was causing problems. Whenever L-110 was not feeding, the unfluidized coal in the line above the feeder would cool and condensate would form. A soft plug of condensate and coal would result and prevent dry coal in the preheater from reaching the feeder. To prevent condensation,

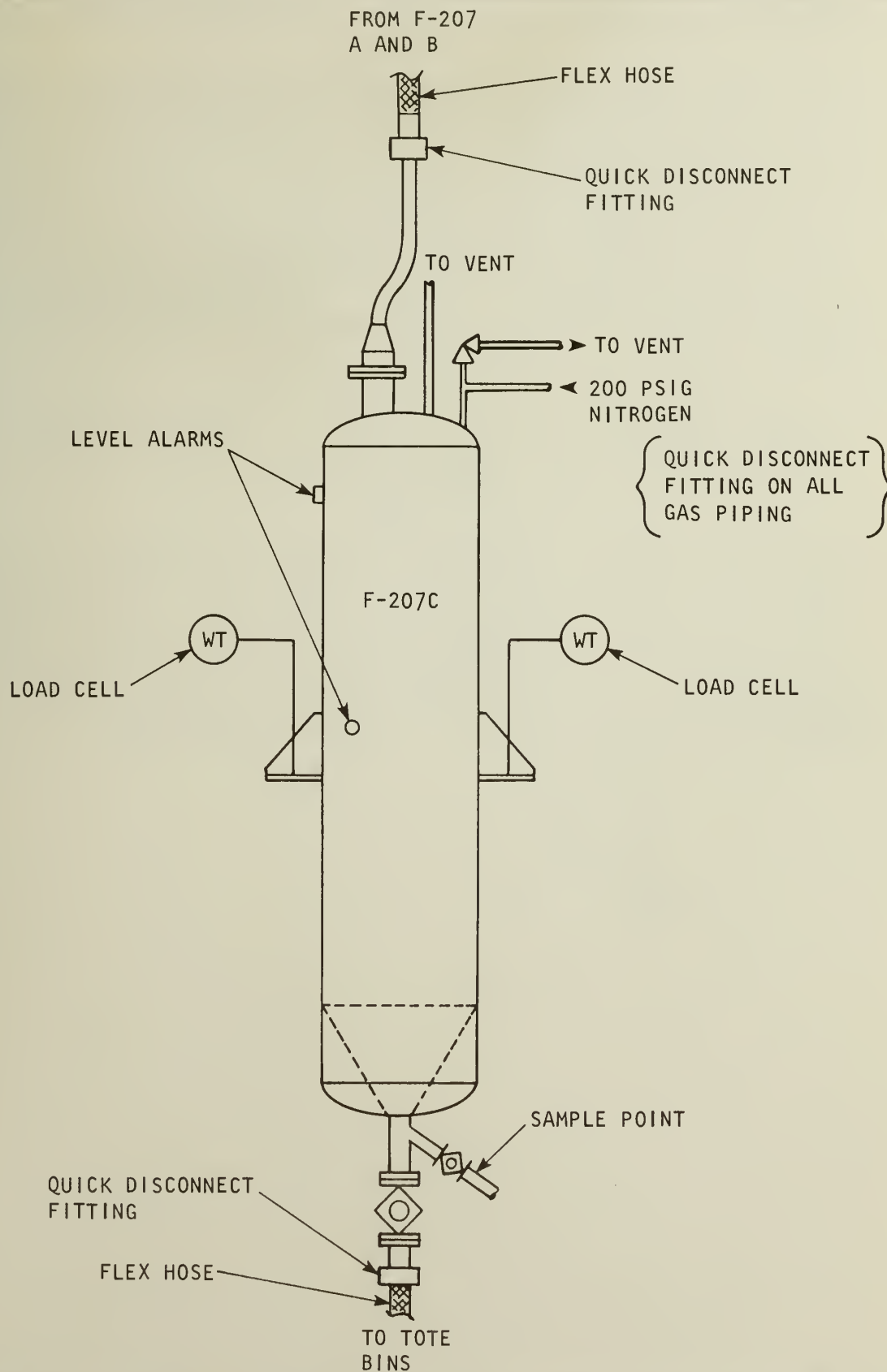


Figure 11-32. F-207C ASH REMOVAL HOPPER

a small steam heat exchanger was installed to heat an inert gas purge that went to the feeder. The hot purge successfully eliminated condensation and the plugs above the feeder.

The problems steam caused at the preheater inlet were slightly different than those it caused above the hot lignite feeder out of the preheater. Since the dry lignite feeder, L-109-L4A, at the preheater inlet, usually fed coal to the preheater at a rate faster than it received coal from the Sweco Screen, L-157, the line above as well as below the feeder was effectively empty. This, coupled with the fact that the preheater operated at a slightly positive pressure with respect to the Sweco screen, quite regularly resulted in steam from the preheater backing up through the feeder and condensing in the Sweco. The condensate and coal in the Sweco would plug the screens, which required shutting down grinding long enough to clean out and dry the Sweco.

The preliminary method to keep the screens clear was to greatly increase the purge between the feeder and the Sweco. During peak grinding periods, the high purge rate would successfully keep steam from the Sweco. However, if grinding slowed or the purge was reduced, the Sweco plugged quickly.

Ultimately, a second dry lignite feeder, L-109-L4B, was installed between the existing feeder and the lignite preheater with the purge between the feeders. As a result, purge gas to the space between the two feeders successfully created a pressure seal that kept the steam in the preheater. Although some purge gas did leak back to the Sweco, it was dry and caused no problems. The L-109-L4 A and B feeders were interlocked such that the lower feeder ran for 30 seconds after the top feeder shut off, to ensure that no coal was allowed to remain between the feeders when not in use. A sketch of the twin feeder setup can be found in Figure 11-33.

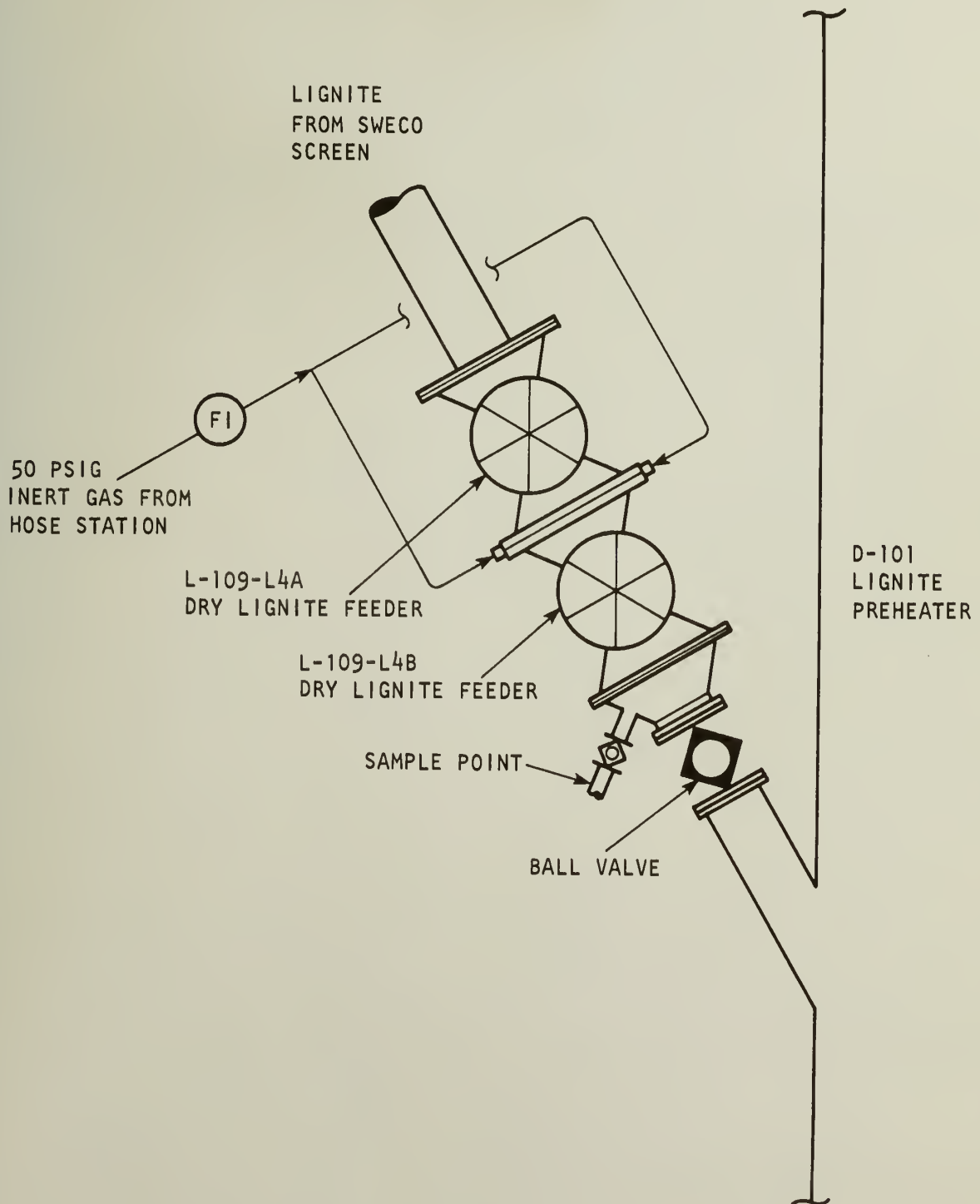


Figure 11-33. DRY LIGNITE FEEDERS

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